PB84-145101

Evaluation of the Disposal of Flue Gas Cleaning Wastes in Coal Mines and at Sea Refined Assessment

Little (Arthur D.), Inc., Cambridge, MA

Prepared for

Industrial Environmental Research Lab.
Research Triangle Park, NC

Jan 84

U.S. Department of Commerce
National Technical Information Service
NTIS

PB84-145101

EPA-600/7-84-005
January 1984

AN EVALUATION OF THE DISPOSAL OF FLUE GAS CLEANING WASTES IN COAL MINES AND AT SEA: REFINED ASSESSMENT

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Prepared for

U. S. ENVIRONMENTAL PROTECTION AGENCY
OFFICE OF RESEARCH AND DEVELOPMENT
WASHINGTON, D. C. 20460

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

TECHNICAL REPORT DATA

(Please read Instructions on the reverse before completing)

1. REPORT NO. EPA-600/7-84-005	2.	3. RECIPIENT'S ACCESSION NO. PB84 145101
4. TITLE AND SUBTITLE An Evaluation of the Disposal of Flue Gas Cleaning Wastes in Coal Mines and at Sea : Refined Assessment		5. REPORT DATE January 1984 6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S) R. R. Lunt, C. B. Cooper, A. S. Reyman, S. L. Johnson, I. Bodek, and W. I. Watson (ADL); and G. C. McLeod and A. J. Barker (NEA)*		8. PERFORMING ORGANIZATION REPORT NO.
9. PERFORMING ORGANIZATION NAME AND ADDRESS Arthur D. Little, Inc. 20 Acorn Park Cambridge, Massachusetts 02140		10. PROGRAM ELEMENT NO. 11. CONTRACT/GRANT NO. 68-03-2334
12. SPONSORING AGENCY NAME AND ADDRESS EPA, Office of Research and Development Industrial Environmental Research Laboratory Research Triangle Park, NC 27711		13. TYPE OF REPORT AND PERIOD COVERED Final; 6/75-9/83 14. SPONSORING AGENCY CODE EPA/600/13

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16. ABSTRACT

The report gives a refined assessment of the feasibility of disposing of flue gas cleaning (FGC) wastes in coal mines and at sea. Its focus is on specific impact areas identified in an earlier assessment. These areas were further investigated through laboratory studies as well as an additional review of published information. For FGC waste disposal in coal mines, the issues addressed are: (1) physical stability of FGC waste deposited in surface mines; (2) effects of freezing on waste dewatering/drainage; (3) fugitive emissions from handling and disposal; (4) leaching of total oxidizable sulfur (TOS) from sulfite-rich wastes; (5) release of gases from waste deposits; and (6) corrosion potential for concrete bulkheads used for containment in underground mines. For disposal of FGC wastes at sea, the impact issues studied were: (1) the physical fate in the water column during descent from conventional barge disposal; (2) benthic transport and sedimentation of dumped FGC waste; and (3) depletion of oxygen due to dissolution of TOS from sulfite-rich wastes. These issues represent potential environmental impacts which may require evaluation for specific disposal conditions. In general, existing controls can mitigate such impacts; e.g., modification of waste properties and waste placement methods.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS		b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group	
Pollution	Assessments	Pollution Control	13B	14B
Flue Gases	Fly Ash	Stationary Sources	21B	
Gas Scrubbing		Flue Gas Cleaning	07A, 13H	
Waste Disposal				
Coal Mines			08I	
Ocean Environments			08J	

18. DISTRIBUTION STATEMENT Release to Public	19. SECURITY CLASS *(This Report)* Unclassified	21. NO. OF PAGES
	20. SECURITY CLASS *(This page)* Unclassified	22. PRICE

EPA Form 2220-1 (9-73)

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

ABSTRACT

This report presents a refined assessment of the feasibility of the disposal of flue gas cleaning (FGC) wastes in coal mines and at sea. It covers the work performed in the second phase of a three-phase program conducted by Arthur D. Little for the Industrial Environmental Research Laboratory of the U.S. Environmental Protection Agency under Contract No. 68-03-2334.

The focus of this refined assessment is on specific impact areas identified in the initial assessment (EPA 600/7-77-051, NTIS No. PB269270). These areas were further investigated through laboratory studies as well as additional review of published information. For FGC waste disposal in coal mines, the issues addressed are: (1) physical stability of FGC waste deposited in surface mines; (2) effects of freezing on waste dewatering/drainage; (3) fugitive emissions from handling and disposal; (4) leaching of Total Oxidizable Sulfur (TOS) from sulfite-rich wastes; (5) release of gases from waste deposits; and (6) corrosion potential for concrete bulkheads used for containment in underground mines. For disposal of FGC wastes at sea, the impact issues studied were: (1) physical fate in the water column during descent from conventional barge disposal; (2) benthic transport and sedimentation of dumped FGC wastes; and (3) depletion of oxygen due to dissolution of TOS from sulfite-rich wastes. All of these issues represent potential environmental impacts which may require evaluation for specific disposal conditions. In general, there are control measures that can be utilized to mitigate such impacts, including modification of waste properties and waste placement methods.

Engineering cost estimates were prepared for several methods of disposal of blended FGD waste and fly ash in surface coal mines, the most promising mine disposal options. Annual, first year costs in 1980 dollars for pit bottom disposal ranged from $2.50-4.50 per metric dry ton for onsite disposal (mine 4 miles from power plant) to $10.00-19.00 for offsite disposal via rail haul (100 to 200 miles one-way). These costs include stackout and handling at the waste processing area through final placement.

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ACKNOWLEDGEMENTS

This study is being conducted by Arthur D. Little, Inc., (ADL) for the U. S. Environmental Protection Agency under Contract No. 68-03-2334. The Edgerton Research Laboratory of the New England Aquarium (NEA) a principal subcontractor to Arthur D. Little, performed the laboratory testing relating to physical impact issues in ocean disposal operations. The report reflects the work of many members of both the Arthur D. Little and New England Aquarium staff. Those participating in the study are listed below:

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Many other individuals and organizations have made significant contributions to this study. In particular, we wish to acknowledge Julian W. Jones, the EPA Project Officer, for his guidance throughout the course of this work and his invaluable assistance in the preparation of this report. We would also like to thank Robert E. Landreth of the Municipal Environmental Research Laboratory, U. S. Environmental Protection Agency for his continuing support and advice; and Jerome Rossoff and Ronald C. Rossi of the Aerospace Corporation and Jerome L. Mahloch of the U. S. Army Engineer Waterways Experiment Station for their cooperation in providing and interpreting data on waste characteristics.

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CONVERSION FACTORS

English/American Units	Metric Equivalent
Length:	
1 inch	2.540 centimeters
1 foot	0.3048 meters
1 fathom	1.829 meters
1 mile (statute)	1.609 kilometers
1 mile (nautical)	1.852 kilometers
Area:	
1 square foot	0.0929 square meters
1 acre	4,047 square meters
Volume:	
1 cubic foot	28.316 liters
1 cubic yard	0.7641 cubic meters
1 gallon	3.785 liters
Weight/Mass:	
1 pound	0.4536 kilograms
1 ton (short)	0.9072 metric tons
Pressure:	
1 pound per square inch	0.07031 kilograms per square centimeter
Concentration:	
1 part per million (weight)	1 milligram per liter
Speed:	
1 knot	1.853 kilometers per hour
Energy/Power:	
1 British Thermal Unit	1,054.8 joules
1 megawatt	3.600×10^9 joules per hour
Temperature Change:	
1 degree Fahrenheit	5/9 degree Centrigrade

I. SUMMARY

A. INTRODUCTION

This is the second in a series of reports on a research program sponsored by the Industrial Environmental Research Laboratory of the U.S. Environmental Protection Agency. The program consists of investigations by Arthur D. Little, Inc. (ADL), the New England Aquarium (NEA), and the University of North Dakota (UND), regarding the feasibility of the disposal of Flue Gas Cleaning (FGC) wastes in mines and at sea. In this program, the FGC wastes studied were wastes from non-recovery Flue Gas Desulfurization (FGD) systems and mixtures of FGD wastes and coal ash.

The first report presented a preliminary assessment performed by ADL of the environmental, technical, regulatory and economic aspects of projected mine and at-sea disposal operations. The purpose of the initial assessment was to evaluate the overall viability and acceptability of disposal and to determine the most promising disposal options and practices.

This second report presents a refinement of the preliminary assessment based upon additional evaluation of selected impact issues identified in the initial effort as requiring further study. The purpose of this refinement therefore, was to acquire additional information necessary to have a more complete understanding of the fate and effects of FGC wastes in coal mine and ocean environments, and a more accurate estimate of the cost of selected disposal operations.

B. PURPOSE AND OBJECTIVES

The purpose of this refined assessment was to acquire additional information needed: (1) to provide a more complete understanding of the fate and effects of FGC wastes in mine and ocean environments; and (2) to allow more accurate estimates of the costs of promising disposal options. Specific objectives were to:

- Perform limited laboratory testing to provide a better insight into the behavior of FGC wastes relating to impact issues for which significant data gaps exist.

- Refine the initial assessment to the extent possible based upon the laboratory test results supplemented by other relevant data and information.

- Prepare engineering estimates of the capital investment and operating costs for representative disposal operations believed to be technically feasible and potentially environmentally acceptable.

While consideration of all aspects of the initial assessment were generally within the scope of this effort, attention was focused on specific physical and chemical impact issues raised in the initial assessment.

C. ASSESSMENT OF DISPOSAL IN COAL MINES

1. Impact Issues Studied

This Initial Assessment study (EPA Report No. 600/7-77-051) indicated that surface coal mines were the most promising sites for in-mine disposal of FGC wastes. That document also reported that while methods for handling and placement of such wastes are available, certain chemical and physical properties of the wastes might have adverse impacts on the environment and/or the operation of the mine being utilized for disposal. Six key chemical and physical impact issues identified in that initial study were subjected to more detailed evaluation in this effort, using information and data obtained from the following sources.

	Information Sources		
Issues	ADL Testing	Independent Testing	Related Information
Physical			
Stability in Surface Mines	-	x	x
Freezing Effects	x	x	x
Fugitive Emissions	-	x	x
Chemical			
Dissolution of Total Oxidizable Sulfur	x	x	-
Offgassing (SO_2/H_2S)	x/-	-/x	-
Concrete Corrosion	-	-	x

The testing performed and the related assessment focused on unstabilized waste because of the lack of definitive data on their behavior. Where possible and appropriate, extrapolation to the potential fate and effects of stabilized wastes has been made.

2. Technical/Environmental Assessment

a. Conclusions

The overall conclusions of the initial assessment are still considered valid. The disposal of FGC wastes in coal mines is feasible from a technical standpoint, and there are practical options available in terms of waste processing, placement and site management to control potential adverse environmental impacts in most cases. However, the viability and environmental impacts of each disposal situation must be evaluated based upon the specific hydrogeology of the site, waste characteristics and placement method.

Specific conclusions regarding the issues and impacts addressed in this refined assessment are discussed below.

(1) Stability - The requirements for physical stability of waste deposits in surface mine disposal operations depend upon the type of disposal operations, the mine characteristics, and the methods of mining employed. In general, it would be expected that most wastes at solid levels near optimum moisture content would have physical and engineering properties adequate to ensure acceptable stability (e.g., resistance to flow under its own weight due to disturbances from mining activities, etc.). In the case of sulfite-rich wastes, this would also certainly necessitate admixture of filtered (or centrifuged) waste with some amount of fly ash. Where the flue gas desulfurization (FGD) waste solids cannot be adequately dewatered and there is unsufficient fly ash available for stabilization, admixture of both fly ash and lime may be required. However, simply the addition of lime may not ensure short-term stability (prior to curing) if the waste is too wet. In such cases, stockpiling of the waste may be required to allow time for curing to begin (which also increases solids content) prior to disposal. Other control measures available, depending upon the type of disposal, to minimize stability problems include: production of gypsum rather than sulfite-rich material; mixing of waste with soil/overburden; control of placement to minimize rewetting (and saturation); and creation of containment walls of overburden either during disposal or after disposal (e.g., by placing the waste in discrete areas or on one side of the pit).

(2) Freeze/Thaw Effects - Freezing of wastes may alter the chemical as well as physical properties of wastes, which can affect handleability and ultimate strength developed. Laboratory testing of untreated waste samples indicated no significant effect of freeze/thaw on drainage of water from the waste. The degree of freezing and the effect of freezing on handleability can be minimized by dewatering (and admixture with ash) to achieve near-optimum moisture content. For areas of the country exhibiting extreme temperature conditions, use of heated trucks may be required (e.g., piping exhaust through truck walls) to ensure handleability.

Freezing would normally be expected to slow curing rates of stabilized wastes. If it occurs prior to the onset of curing, freezing may serverly reduce the ultimate strength achieved. If it occurs after initiation of curing, there may be little or no affect on hardening. In order to increase curing rates and ultimate strength under winter conditions, it may be desirable to stockpile the waste for additional time (4-7 days) to allow onset of curing before disposal.

(3) Fugitive Emissions - Although possible, emission of dust from FGC wastes in mine disposal operations is unlikely due to the relatively high moisture content of the wastes, fugitive dust emissions from stockpiles can be easily controlled. Drying of the waste pile surface will usually result in crustation; however, should dust emissions result, they can be minimized by wetting of the surface in much the same way dirt road surfaces are wetted.

(4) TOS Dissolution - Dissolution of calcium sulfite from sulfite-rich FGD wastes can result in TOS levels in leachates ranging from tens to hundreds of ppm depending upon groundwater ionic strength, acidity and hardness. This can result in levels of chemical oxygen demand (COD) sufficient to deplete dissolved oxygen in groundwater and affect local receiving waters. Where sulfite-rich waste deposits might adversely impact aerobic ground and surface waters, the solubility of TOS should be a consideration in the impact of waste leachate. In many cases, the concentration of TOS, which represents an immediate oxygen demand, may not result in significant reductions in dissolved oxygen due to low leachate rates.

(5) Offgassing Potential - There is potential for offgassing CO_2, SO_2, H_2S and possibly other gases from waste deposits in mines, particularly in underground mines. The release of SO_2 and H_2S is of greatest concern.

SO_2 offgassing can result from contact of neutral or slightly basic, sulfite-rich wastes with highly acidic mine waters (pH $<\sim 3.0$), especially during initial disposal operations where the quantity of waste is relatively small compared to the amount of acid. Longer term evolution of SO_2 is less likely to occur, but also, more difficult to predict as a generalization. The potential for short-term evolution can be minimized by: (1) avoiding placement of sulfite-rich wastes in mine areas containing highly acidic drainage; (2) pumping out and treatment of water prior to placement; (3) preneutralizing water with limestone; or (4) increasing the alkalinity of the waste by admixture of lime or limestone. Minimizing infiltration and/or acidification of groundwater in the mine by: (1) maximum filling of voids; (2) use of bulkheads; or (3) reduction of waste permeability by use of stabilization will also help reduce long-term SO_2 offgassing potential. If the waste is stabilized by admixture of fly ash and lime prior to disposal, additional lime may be required to also negate the effects of the acid water on the curing of the waste.

Release of H_2S from FGD wastes has been noted in a number of instances. Laboratory testing has also indicated the potential for H_2S release. It can occur from either sulfate or sulfite-rich materials due to the activity of sulfate-reducing bacteria. Some of the same measures used to control SO_2 offgassing may also be appropriate for H_2S offgassing. These include: proper selection of disposal sites and disposal methods; waste stabilization prior to disposal; and, in the case of underground disposal, maximum filling of voids and use of bulkheads to reduce contact with water.

(6) Bulkhead Corrosion - Use of bulkheads as containment walls may be required in some areas of underground mine disposal operations. If constructed of concrete they may be susceptible to chemical attack by FGC waste liquors. Deterioration would be expected to be most severe for acidic wastes, especially those containing high levels of dissolved solids (e.g., sodium, magnesium, chloride and sulfate). There was very little information on cement and concrete behavior in the

presence of liquors similar to those that might result from closed-loop operation of FGC systems. Parametric corrosion testing needs to be performed to assess the effects of FGC wastes and to develop a data base sufficient for specifying adequate cement/concrete mixes. Such testing needs to cover realistic and extreme ranges of scrubber liquors and leachate composition. Of particular importance would be concentration of chloride, sulfate, fluoride, sulfite, sodium and magnesium, and pH.

Measures which can minimize the potential for deterioration of concrete bulkheads include: coating of imbedded steel in reinforced structure; reduction in leachate generation by maximum filling of voids and/or waste stabilization and increasing the alkalinity of the waste to avoid developing acidic conditions.

b. Need for Additional Research and Information

Identified research needs include: (1) field-scale demonstration of promising surface mine and underground mine disposal; and (2) monitoring of full-scale ongoing operations to establish practical disposal methods and to evaluate actual environmental impact potential (both detrimental and beneficial). One such demonstration program designed to satisfy both (1) and (2) is currently underway at the Baukol-Noonan mine in Center, ND. This surface mine disposal demonstration program has been funded by the U.S. EPA and DOE and results will be published in separate reports.

Additional testing of waste properties and impact potential under controlled conditions is also desirable to enable a better prediction of disposal requirements and waste behavior. Important among these are the following:

(1) Additional triaxial compression and dynamic load testing on a variety of different wastes (including dry sorbent wastes) and for a range of moisture levels. This will provide a better indication of the degree of dewatering and/or fly ash addition required for disposal of untreated wastes and the effects of variability on handling and stability of the wastes.

(2) Performance of leaching column tests using mine waters and overburden materials to assess potential pollutant mobility in mining environments as well as potential for improvement of mine drainage. This is best performed in concert with demonstration testing or as a part of a full-scale monitoring program. A limited amount of such testing had been performed by Michael Baker, Jr., Inc., Twin City Testing, and the University of North Dakota (as part of the demonstration program at Center, ND).

(3) Performance of testing to evaluate the effects of FGC waste liquors and leachates on cement and concrete.

D. ASSESSMENT OF DISPOSAL AT SEA

1. Impact Issues Studied

Laboratory testing and related assessment efforts with regard to the disposal of FGC wastes focused on three areas:

- Physical fate of wastes in the water column.
- Physical fate of wastes on the ocean bottom.
- Chemical fate of untreated FGC wastes in seawater (i.e., TOS dissolution and oxygen depletion).

2. Technical/Environmental Assessment

a. Conclusions

The two overall conclusions of the initial assessment are still considered valid. These conclusions pointed out the need for case-by-case analysis of disposal and affirmed the technical feasibility of available control options. Other specific initial conclusions have been reinforced by this assessment with some modifications as indicated below.

- Unless further work contradicts observed and anticipated benthic sedimentation impacts including mud flows, the disposal of untreated or treated FGC wastes with soil-like physical properties by bottom-dump barge or outfall on the continental shelf should be considered environmentally undesirable. As noted below, research relating to this option should be continued.

- The problems of disposal of sulfite-rich FGC wastes, both on and off the continental shelf, appear to be much greater than those associated with other FGC materials. There appears to be special grounds for concern over the potential for oxygen depletion in the vicinity of sulfite-rich waste masses. However, direct sulfite toxicity may be a relatively minor issue because of the significant rate of the oxidation reaction.

- Disposal options which still appear promising and are recommended for further research include:
    - dispersed disposal of untreated sulfate-rich FGC waste on the continental shelf;
    - concentrated disposal of treated brick-like FGC waste on the continental shelf;
    - dispersed disposal of treated brick-like FGC waste on the continental shelf;

- dispersed disposal of untreated sulfate-rich FGC wastes in the deep ocean; and

- concentrated disposal of all forms of sulfate-rich FGC wastes in the deep ocean.

b. Need for Additional Research and Information

The following research needs were believed most important in 1977:

- Empirical bioassay data on the acute and/or chronic effects of sulfite-rich FGC wastes on representative marine organisms.

- Empirical bioassay data on the long-term availability and accumulation of FGC waste-related metallic trace contaminants.

- Empirical bioassay data on the suitability of soil-like FGC materials as benthic substrates in quiescent waters.

- The development of empirical data and verified theoretical models to predict field-scale FGC waste behavior during descent through marine water columns.

- Continual investigation of field situations where FGC wastes have entered marine environments.

E. ECONOMIC CONSIDERATIONS FOR MINE DISPOSAL

1. Cases Studied

The following six cases were developed to cover potential combinations of waste type, transportation mode, and in-mine placement for technically promising mine disposal options:

Case E-1. Lime scrubbing with stabilization, onsite mine disposal, Eastern coal.

Case E-2. Limestone scrubbing with fly ash, utilizing forced oxidation, onsite mine disposal, Eastern coal.

Case E-3. Lime scrubbing with stabilization, offsite mine disposal, Eastern coal.

Case E-4. Limestone scrubbing with fly ash, utilizing forced oxidation, offsite mine disposal, Eastern coal.

Case W-1. Limestone scrubbing with fly ash, onsite mine disposal, Western coal.

Case W-2. Limestone scrubbing with fly ash, offsite mine disposal, Western coal.

For each of the six cases, engineering costs were estimated for the loading (at the plant), transport, unloading and placement of the wastes in the mines. Both capital and operating costs were estimated. No estimates were made of certain other elements of the actual overall disposal costs, including any costs associated with the handling and/or processing (thickening, filtration, etc.) operations required prior to transport of the waste to ultimate disposal. The latter costs were not considered unique to mine disposal operations, as they would also be incurred equally for such alternatives as disposal in managed landfills.

2. Results

The estimated per-ton costs for pit-bottom disposal in the six mine disposal cases were as follows:

	$/Ton	
	Wet	Dry
E-1 Lime scrubbing with stabilization, onsite mine disposal, Eastern coal.	2.85	4.40
E-2. Limestone scrubbing with fly ash, forced oxidation, onsite disposal, Eastern coal.	2.25	2.75
E-3. Lime scrubbing with stabilization, offsite mine disposal, Eastern coal.	8.00	12.25
E-4. Limestone scrubbing with fly ash forced oxidation, offsite disposal, Eastern coal.	8.50	10.30
W-1. Limestone scrubbing with fly ash, onsite mine disposal, Western coal.	2.65	3.55
W-2. Limestone scrubbing with fly ash, offsite mine disposal, Western coal.	13.95	18.65

3. Comparison With Other Disposal Costs

The estimated mine disposal costs were compared to transport and placement costs for disposal of similar FGC wastes in managed landfills. This comparison showed that the estimates for the hypothetical onsite mine disposal cases equalled about 75-80% of the typical comparable costs for disposal in managed landfills. Cost savings include the fact that mine disposal would not have the added reclamation cost of a managed fill. However, the estimates for the offsite mine disposal cases were 4-5 times higher than comparable costs for disposal in managed fills. This may be a result of the assumptions of rail-haul requirements of 100- and 200-miles (one-way) for the offsite mine disposal cases, which represent "outer bounds" rather than typical distances to off-site disposal areas. Thus, the estimates and comparisons for the "on-site" cases are probably more realistic than those for the "off-site" cases.

II. INTRODUCTION

This is the second in a series of reports on a research program sponsored by the Industrial Environmental Research Laboratory of the U. S. Environmental Protection Agency. The program consists of investigations by Arthur D. Little, Inc. (ADL), the New England Aquarium (NEA), and the University of North Dakota (UND), regarding the feasibility of the disposal of Flue Gas Cleaning (FGC) wastes in mines and at sea. In this program, the FGC wastes studied were wastes from non-recovery Flue Gas Desulfurization (FGD) systems and mixtures of FGD wastes and coal ash.

The first report presented a preliminary assessment performed by ADL of the environmental, technical, regulatory and economic aspects of projected mine and at-sea disposal operations. The purpose of the initial assessment was to evaluate the overall viability and acceptability of disposal and to determine the most promising disposal options and practices.

Specific objectives of the initial study were to:

- Collect available data on the chemical, physical and engineering properties of FGC wastes in order to provide a data base for the assessment effort.
- Evaluate the potential fate of FGC wastes in mine and ocean environments, including identification of physical, chemical, and biological impacts of concern, and, to the extent possible, determination of realistic disposal criteria.
- Review the state-of-the art of technology related to disposal operations with emphasis on detection, monitoring, and control as appropriate.
- Identify possible benefits that may result from disposal operations.
- Review and assess federal and state regulations focusing on their adequacy for protecting the environment.
- Develop conceptual designs and prepare preliminary estimates of capital and operating costs for representative, feasible disposal operations.

While all aspects of disposal were included in this effort, the principal focus was on environmental impacts.

This second report presents a refinement of the preliminary assessment based upon additional evaluation of selected impact issues identified in the initial effort as requiring further study. The purpose of this refinement therefore, was to acquire additional information necessary to have a more complete understanding of the fate and effects of FGC wastes in coal mine and ocean environments, and a more accurate estimate of the cost of selected disposal operations.

While consideration of all aspects of the initial assessment were generally within the scope of continued consideration in this refinement, attention was focused on specific physical and chemical issues and impacts. These were:

	Issues/Impacts	
Disposal Site	Physical	Chemical
Coal Mine	Waste Stability Freezing Fugitive Emissions	TOS Dissolution Offgassing Potential (SO_2, H_2S) Concrete (Bulkhead) Corrosion
Ocean	Water Column Suspended Materials Long-Term Bottom Transport -Mudflow -Erosion/Resuspension	TOS Dissolution/Oxygen Depletion

This report consists of five chapters and appendices, as follows:

- Chapter I - Summary: describes the issues addressed in this refined assessment, the conclusions and recommendations for additional research.
- Chapter II - Introduction
- Chapter III-Disposal in Coal Mines: provides a discussion of the results of laboratory testing and review of pertinent available information relating to mine disposal issues.
- Chapter IV - Assessment of Disposal at Sea: provide a discussion of the results of laboratory testing and review of pertinent, available information relating to ocean disposal issues and regulations.
- Chapter V-Disposal Economics: presents the engineering cost estimates for selected options for FGC waste disposal in coal mines.

- Appendix A: presents detailed discussions of laboratory tests performed relating to impacts of disposal in coal mines.

- Appendix B: presents detailed discussions of laboratory tests performed relating to impacts of disposal at sea.

- Appendix C: presents detailed discussions of the derivation of a simple mathematical model of the behavior of descending FGC wastes in water.

III. DISPOSAL IN COAL MINES

A. BACKGROUND

1. Impacts and Issues Identified in the Initial Assessment

The initial assessment of the feasibility of disposing of FGC wastes in mines (1) involved a preliminary examination of the environmental, technical, regulatory, and economic aspects relating to mine disposal operations. The purpose of this assessment was to evaluate the overall viability of mine disposal, identify the key issues affecting practicality and acceptability of disposal, and determine the most promising disposal options.

In the preliminary assessment, four principal areas relating to technical feasibility, economic practicality, and environmental impact potential were addressed:

- overall suitability and capacity of various types of mines for accepting FGC wastes;
- disruption of mining operations and impacts deriving from physical instability of the wastes;
- water quality impact potential; and
- air quality impact potential.

The regulatory framework relative to waste disposal and mining operations was also reviewed to evaluate the adequacy of current and pending laws and regulations with regard to mine disposal of FGC wastes.

The approach for the initial assessment involved basically a three-step process:

(1) grouping of mines into general categories according to region, mineral mined, and characteristics (mining method and size), and screening of these categories for capacity and suitability;

(2) for the most promising categories, evaluation of the potential impacts from the placement of unstabilized wastes using convenient/practical disposal methods; and

(3) evaluation of the effects of controlling impacts by limiting or altering waste properties, adjusting placement technique, and/or imposing indirect measures to minimize impact potential.

2. Findings and Conclusions of the Initial Assessment

a. Technical and Environmental Considerations

The overall conclusion from this assessment was that, while promising from both a technological and an environmental standpoint, FGC waste disposal in mines can result in significant environmental impacts; and each proposed FGC waste disposal operation must be assessed on a case-by-case basis to determine the magnitude and acceptability of these impacts. In some cases, positive impacts may be realized from such disposal operations. In assessing the fate of the waste and its potential impacts, consideration must be given to a number of site-specific and waste-specific factors. Important among these are:

- waste chemical and physical properties;
- type of mine and placement techniques;
- local and regional hydrogeology including potential pathways to surface waters;
- groundwater and surface water quality and potential uses; and
- methods for controlling impacts and/or deriving benefits from waste disposal operations.

(1) General Suitability and Capacity Constraints

While there are over 15,000 mines throughout the United States which together are annually producing more than 0.5 billion metric tons of coal and 2.5 billion metric tons of metallic and nonmetallic minerals, much of this capacity is clearly not suitable for FGC waste disposal. A principal factor is the method of mining employed, which in many cases can preclude practical waste disposal operations.

Underground mining which employs caving or cut-and-fill techniques leaves little available void for waste disposal. In open-pit mining, overburden is often removed from the mine area, and the mineral is mined downward from the surface in benches, or the mining operation may follow the ore strata downdip from its surface outcrop, which requires that the area mined be left open for access of haulage vehicles.

In terms of overall technical feasibility, four general mine types offer significant potential for disposal of large quantities of FGC waste:

- surface coal mines;
- underground room-and-pillar coal mines;

- underground room-and-pillar limestone mines; and
- underground room-and-pillar lead/zinc mines.

This selection was based upon an initial screening of major categories of mines, taking into consideration capacity for waste, ease of disposal, prevention of future resource recovery, and general proximity to waste sources. This screening was derived from a national perspective to focus on mine categories of greatest significance; hence, it does not consider small mines that have site-specific conditions favorable to waste disposal.

Of the mine categories listed above, coal mines are the most likely candidates for waste disposal. As a group, they offer the greatest capacity, and they are frequently either adjacent to power plants or are tied directly to a power plant through an existing transportation network. Furthermore, the amount of FGC wastes (both coal ash and wastes from non-recovery FGD systems) resulting from coal combustion is considerably less than the corresponding amount of coal burned. (The quantity of dry waste can typically range from 10% to 40% of the coal burned.)

(2) Disruption of Operations and Physical Stability

The methods used in disposing of FGC waste in mines must be compatible with the mining operation at each site. The placement and handling techniques for disposal of FGC waste are available and demonstrated for storing other materials in mines, although methods may require some modification for application to FGC waste. There is the potential for significant disruption of ongoing mining operations in active mines due to the volume and physical properties of the wastes. Consideration must be given to avoiding or minimizing such disruptions.

In surface mines there are basically three options for waste placement:

- in the working pit, following coal extraction and prior to return of overburden;
- in the spoil banks, after return of the overburden but prior to final reclamation of the land; and
- mixed with or sandwiched between layers of overburden (especially where haulback methods are used for moving overburden).

Truck dumping, such as that used for returning coal refuse, would be the easiest and possibly the only practical method of placement. In an active mine, truck dumping in the pit is probably the most attractive option because it can be accomplished without construction of additional roads or accessways.

In general, the volume of waste disposed of in the mine should not exceed the volume of coal extracted. This would allow returning the mined terrain to roughly the same topographic conditions that existed prior to mining, and it would avoid excessive disruption of mining activities. In most cases, the waste placed in the mine would be only that generated from the coal extracted. However, in some cases, even this amount of waste can cause some disruption and additional handling and placement problems. This could occur in mines with thick coal seams (20-30 m) where the volume of FGD waste may amount to 15-20% or more of the coal burned. In such cases, the average depth of the waste in a pit disposal operation may exceed that achievable through simple truck dumping and may require combined pit bottom and spoil bank disposal or layering operations.

The waste placed in the mine must be relatively dry, with little potential for liquefaction or reslurrying and subsequent flow. A slurry-like or readily liquefiable material would not only make truck transport difficult but could also significantly affect mining activities either during placement or return of overburden (when the increased load of the overburden could cause the waste to flow, resulting in spoil bank slides). This necessitates filtration and probably ash blending or stabilization of wastes from wet scrubbing systems.

In underground room-and-pillar mines, wastes would be most easily placed by hydraulically backfilling slurried waste through boreholes drilled from the surface to the mine void. In active mines, wastes would need to be placed downdip of active mining areas, and bulkheads would probably need to be constructed to prevent flow of the wastes. Pneumatic stowing of very dry wastes (e.g., fly ash) may also be possible, especially in conjunction with longwall mining operations where waste disposal could proceed along with coal extraction (prior to roof collapse).

Placement of wastes in underground mines, particularly stabilized wastes which cure with time to a hardened mass in a manner similar to concrete, may offer some benefits in minimizing roof collapse and long-term subsidence. The degree of long-term subsidence control depends primarily upon the degree to which the mine voids are filled and the compressibility of the waste mass, although to some extent just the presence of the waste may limit the deterioration of support pillars by partially sealing them from air oxidation and groundwater dissolution. If the voids are completely filled with stabilized wastes, it may be possible to essentially eliminate subsidence. However, complete filling of all voids may not be possible, and reduction in subsidence on the order of 30-70% is probably more realistically achievable.

(3) Water Quality

The major potential environmental impact of FGC waste disposal in mines is increased constituents loadings (especially calcium, sodium, and magnesium chlorides and sulfates) in mine drainage discharge. Such discharges can affect both groundwater and surface water quality.

The potential for groundwater contamination due to mine disposal of FGC waste varies with the type of mining technique employed, the climate where the mining occurs, the hydrogeologic conditions of the site, and the characteristics of the waste. In surface coal mines, the degree of leachate production will be a function of whether the groundwater table is above or below the waste layer after disposal. In very deep underground mines, where the confining strata is dense and relatively impermeable because of overlying static loading, groundwater movement is very slow, and the degree of recharge to surface water and wells would be very limited. Disposal of FGC waste in an underground mine which lies well above the groundwater table and is separated from the groundwater table by a relatively impermeable and plastic rock should also have minimal impact.

Leachate production from a waste deposit can be a direct function of the rate of groundwater or infiltration (meteorological) water flow through the deposit. The flow would be limited by the waste (in-place) permeability as well as the surrounding strata permeability depending on which is lower.

Initially, such water will mix with and flush interstitial waste liquors from the deposit. However, it may take tens to hundreds of years for one waste pore volume of groundwater to pass through a given waste deposit. Leachate from waste would move in a plume or a slug through the fractures and solution cavities of underlying strata until it eventually discharged to a downgradient well or surface water. The significance of the leachate would then depend on both baseline groundwater and leachate concentration levels and the use of the downgradient waters.

In general, leachate concentrations would not be expected to be greater than the initial liquor concentrations and, after the first flush, would not exceed equilibrium concentrations (as dictated by groundwater and waste chemistry). According to laboratory testing, most of the total dissolved solids in waste liquor are calcium, magnesium, and sodium chlorides and sulfates, which are not attenuated or precipitated to any significant degree. Only a small amount of the total dissolved solids is attributed to trace elements such as arsenic, boron, cadmium, chromium, copper, lead, mercury, and zinc. In most mine disposal operations, FGC wastes would not be mixed with or placed above a soil matrix which could provide significant, immediate attenuation through cation exchange capacity.

Selenium and chromium are expected to be especially troublesome soluble constituents in leachate because they dominantly appear in the anionic form in the waste and are therefore not affected by cation exchange and cation oxide precipitation mechanisms. Arsenic and boron are expected to leach because they are not readily precipitated, absorption being their primary mechanism of attenuation. Aluminum, beryllium, cadmium, copper, cobalt, iron, lead, manganese, mercury, molybdenum, nickel, and zinc are expected to be partially attenuated by precipitation mechanisms under the neutral to alkaline pH conditions. Where limestone is present, carbonate salts may form with cadmium, copper, iron, lead, and zinc. With acidic background groundwater, potential for precipitation of metals is limited.

While leaching of total dissolved solids and trace elements may be of prime concern, leaching of sulfite or total oxidizable sulfur (TOS) from sulfite-rich wastes is also of concern. Since it is readily oxidized to sulfate, TOS represents an immediate oxygen demand to groundwaters and receiving waters; and TOS may be potentially toxic to aquatic life.

It is important to recognize that, while the leachate composition will be primarily dependent upon the waste characteristics and the groundwater chemistry, other factors may also affect concentrations and speciation in the leachate and downstream groundwater. In addition to general geochemistry and flow mixing, microorganisms in the groundwater and contacted strata can interact with the liquor, catalyzing reactions and affecting overall species balances (e.g., oxidation/reduction).

In certain instances, FGC waste disposal may improve groundwater quality. For example, in mine sites experiencing acid drainage, FGC waste disposal may limit formation of acidity by sealing the reactive pyrite from air exposure and resulting oxidation, and disposal of alkaline FGC wastes may buffer the existing acid drainage.

Surface water contamination can originate along three pathways: groundwater recharge, surface runoff, and mine drainage effluent discharge (pumpout). The extent to which any source is significant can depend on the relative flow of the contaminated source to the assimilating flow of the receiving surface stream within the mixing zone. The chemical constituent contribution of FGC waste to any of the three pathways would be comparable to the levels found in leachate. Therefore, the contributions would not be expected to exceed the initial liquor concentrations during first flush and equilibrium concentrations thereafter.

Based upon the potential water quality impacts of mine disposal of FGC waste and the anticipated regulatory requirements, there are four principal operational parameters that can be used to minimize the significance of impacts to the environment and public health:

- scrubber system operation (waste characteristics);
- waste stabilization;
- site selection (including site geology); and
- placement procedures.

Waste characteristics are largely dependent upon the coal burned, the SO_2 emissions regulations, and the type of scrubber system and the manner in which it is operated. To a limited extent, the basic composition of the waste can be adjusted by choice of scrubber system type. This would include such factors as: wet particulate control versus dry (or simultaneous ash and SO_2 control versus separate ash and SO_2 control); conventional direct slurry scrubbing versus forced oxidation; control of the amount of ash, if any, admixed with the SO_2 scrubbing wastes; and dry sorbent systems versus conventional wet scrubbing.

Both chemical stabilization and compaction serve to increase the dry density of the waste, decrease the waste permeability, and decrease the exposed waste surface area. The improved handling properties of treated wastes should in many cases permit better control of waste placement and better management of the disposal operation.

Site selection can affect not only the amount of leachate produced from FGC waste disposal but also the degree of corresponding groundwater contamination. In general, disposal sites should not have a direct hydraulic connection with a usable water supply, nor should there be a direct connection with small streams having limited assimilative capacity relative to the flow rate of contaminated groundwater. Site selection is also important in terms of influent quality, as it can affect the concentrations of the chemical constituents in the wastes.

Placement procedures can affect the impacts by further isolating the FGC waste from groundwater and surface area (e.g., placement in a surface mine spoil bank) or containing the waste (e.g., bulkheads). Placement in combination with proper site selection and management probably ranks as the most important single method of controlling adverse impacts.

(4) Air Quality

Two types of air quality impacts may be important for mine disposal operations: fugitive emissions of particulate from the wastes, and gaseous emissions from interactions of wastes and mining environments. Fugitive emissions could occur during stockpiling, handling, transport, and placement. The potential for fugitive particulate emissions will depend upon the waste characteristics (especially the degree of dewatering), the site climatology, and the nature of the overall disposal operation.

Potential gaseous emissions include SO_2 and H_2S. SO_2 could be released by contact of acidic mine waters with sulfite-rich wastes, particularly where such wastes are placed in underground mines experiencing acid mine drainage. SO_2 and H_2S could also be released by microbial activity on the waste in the disposal environment.

There has been little research devoted to such emissions. However, the same control measures identified for mitigating water quality impacts might also be applicable to avoiding such air quality impacts.

In addition to these potential adverse impacts, the disposal of FGC wastes may have some potential side benefits with regard to air quality. One such benefit in underground mine disposal could be prevention of mine fires.

b. Need for Additional Research and Information

The following research needs were believed most important in 1977:

- Development of additional, more comprehensive physical and engineering properties data base and corroboration (or comparison) of results with field data. Of particular interest are:
    - triaxial compression tests for shear strength of untreated sludges to determine the ability to support loadings while unconfined;
    - dynamic triaxial compression tests for untreated sludges to simulate resistance to shear under seismic cyclic loadings applicable to various regions of coal reserves;
    - consolidation tests for untreated and soil-like treated sludges to simulate density and permeability under various static loadings related to overburden pressures; and
    - Atterberg limits for untreated sludges.

  Some of this testing was underway in programs funded by EPA and other governmental agencies and will be reviewed as available as a part of the continuing assessment effort.

- Development of a data base on key chemical impact issues relating to mine disposal. Of particular importance are:
    - the potential for TOS leaching from sludges and rates of TOS oxidation;
    - the potential for chemical attack of cement/concrete by sludge liquors and leachate;

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- the potential for SO_2 evolution (during the initial stages of sludge disposal in underground mines with acidic environments) and H_2S production; and
- the short-term effects of climate (e.g., freezing, excessive rainfall, etc.) on the physical properties of untreated sludges and pollutant mobility.

3. Purpose, Scope, and Approach of This Refined Assessment

The preliminary assessment of FGC waste disposal in mines identified a number of issues and impact areas as needing further study in order to gain a more complete understanding of the potential behavior of FGC wastes in mine environments. The purpose of this refined assessment, therefore, was to acquire additional information necessary for a more accurate description of the fate and effects of FGC wastes in mine disposal operations. The objectives were to:

- perform limited laboratory testing to provide a better insight into the behavior of FGC wastes relating to impact issues for which significant data gaps exist;
- based upon the laboratory test results supplemented by other, new, relevant data and information, refine the initial impact assessment to the extent possible; and
- prepare engineering estimates of the capital investment and operating costs for representative disposal operations believed to be technically feasible and potentially environmentally acceptable.

While all aspects of the initial assessment were generally within the scope of continued consideration, attention was focused on six specific physical and chemical impact issues raised in the initial assessment. These were:

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Physical Impact Issues

(1) Physical stability in surface mine disposal
(2) Freezing effects
(3) Fugitive particulate emissions

Chemical Impact Issues

(1) TOS dissolution/oxidation potential
(2) SO_2 offgassing (and H_2S offgassing)
(3) Potential for corrosion of concrete bulkheads

This work concentrated on unstabilized wastes because of the lack of definitive data on their behavior. Where possible and appropriate, extrapolation to the potential fate and effects of stabilized wastes has been made.

Table III-1 summarizes the information sources and the testing performed. Three of the impact issues were investigated in laboratory testing--freezing effects, TOS dissolution oxidation, and SO_2 offgassing potential. These are three areas where there has been little published information and where limited laboratory studies can provide some indication of the behavior of FGC wastes. In all three areas, laboratory testing was designed to evaluate the behavior of sulfite-rich wastes. The suite of samples used, shown in Table III-2, included wastes from direct lime and limestone scrubbing, and a dual alkali system. The results of this experimental work was supplemented by additional information as indicated in Table III-1. Details of testing are provided in Appendix A.

No in-house laboratory testing was performed with regard to the other three areas of impacts noted above--physical stability, fugitive particulate emissions, and corrosion potential. The extent of laboratory testing

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TABLE III-1

SUMMARY OF TESTING AND INFORMATION SOURCES

	In-House Laboratory Testing	Independent Laboratory and/or Field Testing	Related Published Information and Industry Contacts
Physical Impact Issues			
(1) Physical Stability	---	✓	✓
(2) Freezing Effects	✓	✓	✓
(3) Fugitive Particulate Emissions	---	✓	✓
Chemical Impact Issues			
(1) TOS Dissolution/Oxidation	✓	✓	---
(2) SO_2 Offgassing/H_2S Offgassing	✓	---	---
(3) Concrete Corrosion Potential	---	---	✓

Source: Arthur D. Little, Inc.

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TABLE III-2

MAJOR CONSTITUENTS IN FGC WASTE SAMPLES USED IN LABORATORY TESTING

Process	Sample Designation	Form	Type	Wt % Solids	Chemical Analysis						Acid Insolubles	Tests Used		
					Ca	Mg	Na	TOS	SO_4	Cl		TOS Dissolution	SO_2 Offgassing	Freezing
					(m mols/dry gram)						(wt %)			
Dual Alkali	DA2	Filter Cake	Sulfite-Rich	62	(7.2)	0.2	0.4	(5.9)	(1.0)	(0.04)	nil	✓	✓	✓
	DA3	Filter Cake	Sulfite-Rich	57	4.43	0.22	0.22	2.66	0.87	0.03	31	✓	---	---
Direct Lime	L1	Centrifuge Cake	Sulfite-Rich	66	4.59	0.05	0.03	3.85	0.70	0.05	35	✓	---	✓
	L2	Filter Cake	Sulfite-Rich	55	7.22	0.07	0.03	5.76	1.37	0.03	1	✓	✓	✓
Direct Limestone	LS_2	Settled Slurry	Sulfite-Rich	58	6.48	0.07	0.03	3.04	0.64	0.09	25	---	---	✓

Source: Arthur D. Little, Inc.

required to allow a preliminary evaluation of these issues was beyond the scope of this study. Therefore, efforts were directed toward updating and extending the information base developed in the assessment, relying principally on ongoing testing of FGC wastes and waste disposal monitoring programs.

B. REFINEMENT OF THE ENVIRONMENTAL ASSESSMENT

1. Physical Fate/Effects

a. Physical Stability

The requirements for stability of FGC waste deposits in surface mine disposal operations will be dictated by the mode of disposal, manner of waste placement, the mine characteristics and the mining method employed. In some cases, the requirements can be considerably less stringent than in other land disposal practices.

(1) Surface Mine Disposal Options

For surface mine disposal, wastes must be deposited as relatively dry, soil-like materials. A number of disposal modes are possible:

- in the pit bottom prior to return of overburden;
- mixed with or sandwiched between layers of overburden (especially where dozers and shovels are used for back-filling);
- in spoil banks (vee-notches) before rough contouring; and possibly
- after contouring and before or during replacement of top-soil.

In each case, the minimum requirements for stability and waste handling properties will differ.

For disposal in pit bottoms, it is important that the waste deposit be sufficiently stable that it not flow under static loadings created by the weight of overburden, or its own weight, and that it not flow under dynamic loading conditions created by mining operations (e.g., machinery vibrations, replacement of overburden, blasting) and natural phenomena (e.g., seismic disturbances). Placement of the waste in a pit bottom should not result in interference with ongoing waste disposal or mining activities either directly by flowing into the active mining area or indirectly by causing overburden slides.

Spreading and compaction of wastes prior to return of overburden should generally not be necessary as normal practice unless stabilization (hardening) is required for environmental (or physical stability) reasons, or unless the volume of waste is large enough to require layering. In most eastern and interior mines, layering would not be expected to be necessary. Coal seam thicknesses in eastern, interior and many western surface mines rarely exceed about 10 feet on the average. The volume of FGC wastes (FGD waste and coal ash) would generally amount to less than 50% of the volume of coal extracted except for very high sulfur and/or high ash coals.

Stabilization by admixture with fly ash and lime, though, is one option for providing both short-term and long-term stability. An alternative is controlled placement of the waste. One approach is to pile the waste by rear-dump truck on the side of the pit farthest from the next cut. Then, when the overburden is replaced, there will be a boundary of overburden between the waste and coal extraction in succeeding strips.

Another approach is to layer or mix the waste with overburden. This is most appropriate for operations where overburden is returned by dozers and shovels. The requirements of physical stability will then depend upon the relative quantities of overburden and waste. In general, where the amount of overburden is considerably greater than the waste, the physical properties of the waste will be dictated by handling requirements.

In spoil-bank disposal operations, the likelihood of the need for spreading and compacting of the wastes in layers is greater than in pit bottoms because of the smaller area available. The vee-notches between the spoil banks would need to be leveled to provide a rough access way for trucks; however, more extensive preparation work would be costly and time-consuming. Thus, if the volume of waste resulted in an average deposit depth significantly greater than that achievable by rear-dump vehicles, then layering of the wastes would be required. If this were the case, then the wastes must have properties adequate for handling with conventional earth-moving equipment.

As a minimum, were spreading not required, the waste piles as dumped must have sufficient stability (or develop sufficient strength) that they will not flow under static loading or due to vibrations from seismic disturbances and machinery. Such stability requirements for vee-notch disposal would be expected to be less stringent than in pit-bottom disposal. There is little likelihood that the wastes will directly impact the coal mining activities. The spoil banks themselves provide natural constraints to the movement of the waste and, if necessary, interim dikes or containment walls can be constructed of overburden or soil at interim points along the vee-notch to minimize potential waste instability impacts on continuing disposal operations. Leveling of the spoil banks after disposal would also be expected to present less dynamic load on the waste than the dumping of overburden on wastes deposited in pit bottoms.

FGC waste disposal on top of the overburden, prior to covering with top soil, would, of necessity, require spreading and, possibly, compaction and layering, depending upon the land area utilized for disposal. This type of operation could resemble that of a dry impoundment, except that the depth of the waste deposit and number of layers of lifts would be expected to be considerably less. However, long-term stability of the waste deposit would still be a concern in this type of disposal (in general, much more so than in spoil-bank and vee-notch) because of the proximity of the waste to surface activities and the lesser degree of natural containment.

(2) Waste Properties

Waste physical and engineering properties that are important to both short-term stability requirements (during disposal and reclamation) and long-term stability are:

- consistency-water content
- moisture-density (compaction)
- compressibility (consolidation)
- strength parameters
  - unconfined compressive strength
  - confined (triaxial) compressive strength
  - sensitivity (ratio of undisturbed strength to disturbed strength).

A laboratory investigation of these properties was beyond the scope of this study. However, physical and engineering properties data available from other sources including work then underway were reviewed and evaluated. The principal focus of this effort was on untreated (unstabilized) wastes, namely FGD wastes and FGD waste/fly ash mixtures. Treatment of the wastes to produce a material which will cure with time into a hardened mass can be effected if necessary for stability and/or environmental impact control; however, it can be considerably more expensive than disposal of untreated waste. The cost of lime alone (if used as a stabilization additive) can amount to more than $2.00/dry ton of waste (total ash and FGD).

The most comprehensive testing of the physical and engineering properties of untreated FGC wastes had been performed by the University of Louisville (UL) (2-7) and Radian Corporation (Radian) (8). Laboratory studies conducted by UL and Radian have provided much of the strength-related data currently available for both untreated and stabilized FGC wastes including sulfite- and sulfate-rich materials. More limited laboratory testing of engineering properties has been performed by a number of other organizations. Prominent among these are studies by Aerospace Corporation (Aerospace) (9, 10); Hass and Ladd (11); Klym and Dodd (12); FMC Corporation (13, 14); U.S. Army Waterways Experiment Station (WES) (15); Twin City Testing (TCT) (16); The Southern Company Services (17, 18); and Arthur D. Little (ADL) (19). Table III-3 lists the laboratory investigations of stability- and strength-related properties by these organizations.

The data from these studies have been reviewed by ADL in a report to EPA (21) and, therefore, will not be discussed here in detail. However, a summary of the data will be presented and the implications for surface mine disposal discussed.

TABLE III-3

PUBLISHED INVESTIGATIONS OF PHYSICAL PROPERTIES RELATED TO STABILITY IN SURFACE MINES

	Type of Waste		
Physical/Structural Properties	Sulfite-Rich	Mixed	Sulfate-Rich
Unconfined Compression Tests	Radian (8) UL (2, 4, 5) ADL (19)	H&L (10) K&D (11)	Radian (8) TCT (16) ADL (19)
Compaction	FMC (13, 14) SCS (17. 18) UL (2, 4) WES (15) ADL (19)	H&L (11) K&D (12) UL (2) WES (15)	SCS (17) TCT (16) UL (2, 5) WES (15) ADL (19)
Consolidation	Dravo (20) FMC (14) SCS (17, 18) UL (5)	UL (5, 7)	UL (6, 7)
Triaxial Compression	FMC (13, 14) Radian (8) UL (2)	H&L (11) K&D (12)	Radian (8) UL (2-6)
Dynamic Loading	SCS (17, 18) UL (6)		
Atterburg Limits	Dravo (20) FMC (13, 14) UL (2)	H&L (11) K&D (12) UL (71)	UL (2-6)

Source: Arthur D. Little, Inc.

Consistency-Water Content

Consistency can be generally viewed as the stiffness of a material and is a function of the water content and particle size and morphology. Atterburg Limits tests provide one measure of the consistency of a material. The liquid limit is the water content above which (or solids content below which) a material behaves as a viscous fluid; conversely, the plastic limit is the water content below which (or solids content above which) a material behaves as a semi-solid. Between these values, a material behaves as a plastic (remoldable) material.

Most in-place cohesive soils (e.g., clays) exhibit plastic characteristics because of their water content. On the other hand, granular soils (e.g., sands and silts) are generally nonplastic--that is, at a certain water content value they transform from a semi-solid material to a viscous liquid. Therefore, Atterburg Limits tests are only meaningful for clay-like or reasonably cohesive materials.

FGC wastes (FGD wastes and mixed FGD waste and ash) are similar to silts and sandy silts with regard to their particle size distribution; thus, untreated FGC wastes would be expected to exhibit little or no plasticity (plastic limit). In fact, testing of a number of different sulfite- and sulfate-rich FGD wastes--both with and without fly ash--indicate that only a few samples exhibit plastic behavior. Pseudo-liquid limits were determined for a number of sulfite-rich materials (2, 4, 5); however, these are water content values at which behavior transforms from that of a semi-solid to a viscous fluid. While the available data on these pseudo-liquid limits are sketchy, there are some interesting trends:

- For the samples tested (from one direct lime and two dual alkali systems), the liquid limits for FGD waste alone and mixed with fly ash or fly ash and lime (uncured) were measured in the range of 33-65% moisture (61-75% solids on a total weight basis).

- The liquid limit tended to decrease (in terms of moisture content) with increasing fly ash content.

- And, the dual alkali wastes exhibited higher liquid limits (higher moisture content at which liquefaction occurs) than the direct lime sample.

While it is clear that the solids content of the wastes must be above the liquid limit, that alone is not sufficient for quantitative information on the potential behavior of FGC wastes. Liquid limit and plastic limit values are useful only to the extent that they correlate with engineering properties employed in design. As previously mentioned, Atterburg Limits strictly apply only to cohesive materials; further, the direct relationship of liquid and plastic limit values to compressibility and strength of FGC wastes has not been demonstrated.

Moisture-Density (Compaction)

Compaction tests yield data on the optimum water content of the material. The density of the waste as placed influences the degree of settlement, permeability and in-place strength. Data on maximum dry density and optimum moisture content (and corresponding degree of saturation) are obtained from Proctor compaction tests. Such tests have been performed on FGC wastes by more than a half-dozen organizations (2, 4, 5, 11-17, 19).

Testing of sulfite-rich waste samples without ash, from four different FGD systems, yielded maximum dry densities ranging from 1.15 to 1.36 gms/cc, with a median value of 1.28 gms/cc. The corresponding optimum moisture content typically ranged from 32-43% moisture, dry basis (70-76% solids), and the percent saturation ranged from 69-91%. In general, addition of fly ash, or fly ash and lime, increased the maximum dry densities and decreased both the moisture content and percent saturation at the maximum dry density. This is to be expected since: (1) fly ash has a slightly higher range of maximum dry densities (1.14-1.65 gms/cm^3) with lower optimum moisture contents (16-31%); and (2) the differences in particle morphology between ash (spherical) and FGD wastes (platelets, needles, or agglomerates) allow displacement of water between stacked crystals by the ash.

Sulfate-rich wastes exhibited maximum dry densities of 1.12-1.52 gms/cc with corresponding moisture content of 13-33% (75-88% solids). However, many of the samples tested did not have well-defined maxima. Addition of fly ash to sulfate-rich wastes also generally increased the maximum dry density and decreased the optimum moisture content; however, unlike the sulfite-rich wastes, the level of saturation at maximum density remained relatively unchanged.

In order to study the effects of repeated working of sulfite-rich waste on compaction properties, UL retested samples of dual alkali wastes which were previously compacted. The maximum dry density increased by about 10%, from 1.15 to 1.28 gms/cc, and the optimum moisture content decreased from 33% moisture (75% solids) to 30% moisture (77% solids)--possibly indicating breakdown of some of the waste particles.

Very little information is available on field compaction behavior of FGC wastes under controlled conditions which can be used to correlate laboratory and field moisture-density relationships. However, it would be expected that the maximum dry densities achievable in field compaction operations would be lower than in Standard Proctor compaction tests.

Strength Parameters

The strength and compressibility of a soil-like material such as FGD waste are a function of the nature of the solid particles (i.e., density, morphology, grain size distribution and intergranular attractive forces) and the amount of water present. Pressure applied to a sample will be transmitted both to the water within the pores between solid particles and to the structural framework of the solids. The behavior of the material depends upon the magnitude of the resultant water pressure and the intergranular (grain-to-grain) pressure. The pressure exerted from grain to grain is called the effective pressure or effective stress, and it determines the strength and compressibility relationships. If the external pressure is carried entirely by the water within the voids, the material will not compress and the strength of the material under increased load will be the same as the strength under lower confining pressures. If, on the other hand, the grain-to-grain pressure is increased, the sample will decrease in volume and the strength of the compressed material will be higher than that of the original material, or the material under lower confining pressure.

Both volume change (compressibility) and strength of FGC waste deposits (or piles) are important. The compressibility describes the change in waste density (and volume) due to consolidation (settlement under its own load) and/or external loads.

Compressibility is of particular interest with regard to large impoundment areas, especially deposits which are fairly deep and near the surface of the mine.

To date, there has been only a limited amount of consolidation testing performed on FGC wastes. The most comprehensive work has been performed by UL (5, 6, 7). This work involved testing of two sulfite-rich waste samples with and without fly ash and two sulfate-rich waste samples. Some data are also available from other studies (14, 17, 18, 20).

In general, consolidation test results indicate that untreated FGC wastes are likely to be very compressible unless the solids content of the waste is increased to near optimum moisture content by dewatering and/or addition of dry fly ash. As would be expected, compaction prior to consolidation testing also significantly decreases compressibility of dewatered wastes.

Settlement of soil-like materials under load usually involves two different phases of consolidation--primary consolidation and secondary consolidation. With the FGC wastes tested by UL, complete primary consolidation occurred within the first minute--much more quickly than with most soils--and it occurred most rapidly in wastes with the lowest moisture content.

The two most important parameters relating to consolidation determined in consolidation tests are the compression index, C_c, which is a measure of the total settlement that can occur, and the coefficient of consolidation, C_v, which is a measure of the rate at which settlement occurs. The ultimate settlement of a compressible material under an increase in stress, $\Delta\sigma$, is given by:

$$S_u = \frac{C_c L}{1 + e_o} \log_{10} \frac{\sigma_o + \Delta\sigma}{\sigma_o}$$

where L = thickness of the layer

e_o = void ratio at σ_o

σ_o = stress carried prior to the imposition.

Therefore, C_c is the slope of the consolidation curve.

In general, C_c increases with increasing stress ranges and with increasing moisture content. For three different samples of untreated sulfite-rich FGD wastes without fly ash dewatered to solids levels similar to filter cakes (43-63 wt % solids), measured values of C_c varied from 0.12-0.3 for a stress range of 24-48 kN/m^2 (500-1000 psf), up to 0.58-1.15 for a stress range of 480-960 kN/m^2 (10,000-20,000 psf). Increasing the solids content of the wastes to greater than 75% solids by additional dewatering or addition of fly ash and, in some cases, compaction reduced the compression indices to the range of 0.02 to 0.16 over the same ranges of stress.

Sulfate-rich waste showed lower compressibility. Two samples of gypsum from forced oxidation-type systems at solids contents of 71-88% had compressibility indices of 0.01 to 0.02 at stress ranges of 24-48 kN/m^2, and 0.03 to 0.12 at stress ranges of 480-960 kN/m^2. While these compressibilities are in the same range as those obtained with some sulfite-rich wastes at equivalent solids levels (i.e., dual alkali wastes), it should be noted that this range of solids contents can be readily achieved with sulfate-rich wastes by standard dewatering practices.

Determination of the coefficients of consolidation, C_v, for untreated FGC wastes using standard deformation-time data is difficult because primary consolidation occurs so rapidly (usually less than 30 seconds). Using both triaxial compression data as well as one-dimensional load tests, rough estimates have been obtained for the coefficients of primary consolidation for three samples. These ranged from 0.25-1.2 in^2/min for a direct lime slurry scrubbing sample, to about 3.0 in^2/min for dual alkali and gypsum samples. Hence, settlement of these latter wastes would be expected to occur 5 to 10 times faster than settlement of the direct lime waste tested.

Thus, depending upon the nature of the waste, the depth of the deposit, and the load applied, the degree of consolidation could range from a few inches or less up to 5% or more of the waste depth, and completion of consolidation may require as little as a few weeks or as long as a year. In pit-bottom disposal, where large quantities of overburden are placed on the waste deposit, consolidation would be expected to occur relatively rapidly, being nearly complete before surface reclamation. If, on the other hand, wastes were spread on top of the returned overburden, then consolidation would be a consideration in future land use. In such cases, consolidation could be controlled if necessary by mixing the wastes (especially sulfite-rich) with fly ash and by compaction as in a standard landfill operation.

The strength characteristics of a waste deposit are best predicted by triaxial compression tests. Such tests provide information on the relationship of strength to cohesion and shear stress as defined by:

$$S = C + p \tan \phi$$

where S = shear strength

C = cohesion

ϕ = the angle of internal friction, which relates shear strength to intergranular pressure, p.

In general, cohesion is an indication of the strength of a material under low load (e.g., relatively thin waste deposits) and the angle of internal friction is an indication of the steepness and depth allowable in a deposit. For example, a material with some cohesive strength but a low angle of internal friction may have sufficient stability in thin deposits under its own load but may fail in deep deposits because the strength at the bottom of the deposit is exceeded by the stress.

Clayey soils and fine-grained materials generally have cohesive strength and low angles of internal friction. That is, strength increases only slightly with increasing stress. Coarse-grained sand, on the other hand, has little or no cohesion but significantly higher angles of internal friction. By comparison, cement has a very high cohesive strength and essentially a zero angle of internal friction (strength independent of stress). Most sulfite- and sulfate-rich FGC wastes resemble micaceous silts and fine sands in shearing behavior. They possess low, if any, effective cohesion (0-5 psi) and angles of internal friction of 30-42° (2-6). As would be expected, the effective cohesion decreases and the angle of internal friction increases with larger particle sizes, such as those produced in some dual alkali (sulfite-rich) and forced oxidation (sulfate-rich) systems. Addition of fly ash to dewatered FGD wastes usually results in increases in effective cohesion (up to 10-15 psi and slightly higher) and, in most cases, decreases the angle of internal friction. However, fly ash can also increase the angle of internal friction for wastes exhibiting low values ($\sim$30°).

The cohesionless nature of FGD wastes can lead to loss of stability or liquefaction under load or when subjected to vibration. The effects of vibratory loading on two FGD wastes were tested by UL (6). Model embankments created of layers compacted at 20% of Standard Proctor with side slopes of 25° were subjected to horizontal vibration on a shake table. Test results indicated a significant failure potential for wastes with solids levels below optimum moisture content with loadings (amplitude and frequency) simulating those which would be created by seismic disturbances, blasting, etc.

(3) Stability Considerations

Limitations on the physical and engineering properties of wastes required for handling and unloading may not be sufficient to ensure stability. This is particularly true if wastes are to be layered and compacted.

As a minimum, the solids content of the waste placed in the mine should approach the optimum moisture content. This should ensure not only adequate handling and placement properties, but also minimize potential for liquefaction. For sulfite-rich and some sulfate-rich wastes, this may necessitate admixture with fly ash following some degree of dewatering. In most cases, sulfite-rich wastes will require vacuum filtration or centrifugation. For some sulfate-rich wastes admixed with fly ash, dewatering beyond thickening may not be required, especially in low sulfur, high ash coal situations. Where gypsum is produced by forced oxidation, and for some sulfate-rich wastes produced by conventional systems, admixture with fly ash may not be required. Filtration or centrifugation may increase the solids levels of these wastes close to the optimum moisture content.

There are many instances where it is not possible to achieve optimum moisture levels due either to the nature (dewaterability) of the FGD waste and/or to an insufficient quantity of fly ash. Variabilities in the operation of the FGD and waste dewatering systems are also certain to occur, as are fluctuations in the ash and sulfur content of the coal--all of which can affect the nature of the FGD waste as well as the relative quantities of wastes available.

There are a number of options for controlling or avoiding potential stability problems in such instances: modification of the FGD waste characteristics; additional processing of the wastes (stabilization); and control of waste placement and disposal operations. Specific control measures include:

- stabilization by admixture of lime (and fly ash) with layering and compaction;
- mixing of the waste with soil during return of overburden and/or reclamation (this is particularly suitable for mines using shovels and bulldozers for overburden placement);
- modification of FGD operations to produce gypsum or increase the sulfate content of the wastes (for mixed sulfite/sulfate wastes);
- placement of the wastes to minimize rewetting and avoid saturation by contact with groundwater, mine runoff or drainage; and

- creation of overburden containment walls in pit-bottom disposal either by construction of berms or placement of waste piles on one side of the strip prior to overburden return.

b. Freeze/Thaw

Very little attention had been given to the effects of weathering (freeze/thaw and/or wet/dry cycles) on the physical properties of FGC waste deposits and the subsequent environmental impacts. Freezing of wastes and freeze/thaw cycles are of particular interest. In many parts of the country, freezing of wastes is certain to occur during handling and transport and/or soon after placement if disposal is continued year-round. Where extensive freezing occurs, it can significantly affect the characteristics of the waste deposit through both physical and chemical alterations. The effects, though, may be beneficial as well as detrimental in terms of alteration of the wastes and/or potential environmental impacts.

For FGC wastes (or soil-like materials) to freeze, three conditions must be met. The material must have:

- a frost-susceptible grain size distribution;
- a freezing temperature; and
- a supply of interstitial water.

Soils, for example, are usually frost-susceptible when more than 3% of the particles are finer than 0.02 mm (22). Thus, fine sands and silts are particularly susceptible to frost, and most FGC wastes would be expected to be susceptible to frost. For a number of soils, especially silts and silty soils, ice formation of layers increases the overall soil volume far beyond the normal 9% water volume increase expected from freezes.

Some of the possible effects that freezing and freeze/thaw cycles can have on FGC wastes are:

- difficulty in transport, handling, and placement;
- for stabilized wastes (fly ash/lime/FGD mixtures) enhancement or inhibition of stabilization reactions resulting in either improved or lessened final strengths. This could lead to variability in the properties of waste deposits; and
- improved drainage/dewatering of wastes releasing occluded liquor or absorption of additional water resulting in higher moisture contents and increased waste volumes.

In surface mine disposal operations, freezing and freeze/thaw cycles can occur during storage/handling/transport, and during and after placement, especially if the waste remains exposed prior to return of overburden or final contouring of the spoil banks. There is little likelihood of freezing of the wastes in underground mine disposal operations except during storage and transport. In either case, disposal operations can be designed to avoid or minimize freezing during storage and transport.

Testing of freezing and freeze/thaw effects has been conducted by the University of Louisville and Louisville Gas and Electric (23), Radian (8), and by Arthur D. Little as a part of this program. The focus of the testing in each of the studies was different. The work performed in this program involved the determination of freezing points and the effect of freeze/thaw cycles on the dewaterability of untreated wastes. The Radian study focused on the effects of freeze/thaw cycles on the curing and strength of stabilized FGC wastes. The work performed by the University of Louisville and Louisville Gas and Electric also focused on stabilized wastes. Each of these studies and the significant results are discussed below.

(1) Effects on Untreated Wastes--ADL Laboratory Testing

Laboratory testing was conducted to confirm the approximate range of temperatures for which different types of FGC wastes freeze and to determine whether there is any potential for significant loss of occluded liquor upon thawing. Freezing points were determined for two sulfite-rich waste samples--a centrifuge cake from a direct lime system and settled slurry from a limestone system--from cooling curves after each sample was immersed in a -8°C bath. Freeze/thaw tests were performed on four sulfite-rich waste samples--a centrifuge and filter cake from a direct lime system, the settled slurry from the limestone system, and a filter cake from a dual alkali system--at two temperatures (-24°C and -8°C).

The freezing point of direct lime centrifuge cake was determined to be -1.0°C, which corresponds to the freezing point of a 0.25 M Na_2SO_4 solution. The freezing point of the limestone waste was found to be -0.5°C, corresponding to a solution concentration fo 0.11 M Na_2SO_4. These freezing point ranges were predictable based upon the concentration of the solutes. Substantial supercooling was observed (to -4°C) before the wastes froze. Both frozen samples contained multiple crystallization lines indicative of very rapid freezing (due to supercooling).

Freeze/thaw tests were performed on the three direct scrubbing system waste samples as received. Samples of dual alkali waste were frozen both as packed samples (packing density = 1.4 gm/cc) and as loose samples (packing density = 0.76 gm/cc). The packed samples yielded a hard mass, while the loose samples could be pried apart with a spatula. No liquid layer appeared on the surface of any frozen as-received waste. The dewatering experiments were designed to examine the difference in the ability of wastes to retain water after one freeze/thaw cycle compared with as-received wastes. Dewatering characteristics were determined by placing the waste in a Buchner funnel equipped with a filter paper and a flexible rubber dam (which prevented air from passing through the sample and served to exert uniform pressure on the surface of the wet thawed waste). Suction was applied for ten minutes, and the amount of water released was measured by weighing the receiving flask before and after suction.

Table III-4 lists the results of the dewatering experiments. No substantial difference in dewatering occurred after one freeze/thaw cycle (employing freezing temperatures of -24°C and -8°C) except in the case of dual alkali waste to which water had been added, where the amount of water released after the freeze/thaw cycle was higher than from the as-received sample. In all other cases, the amount of water released and the percent solids remaining after freeze/thaw and suction were similar to the values obtained for samples which had not been frozen. The dewatering of dual alkali waste samples after freeze/thaw was not affected by the degree of packing employed.

In summary, the laboratory testing conducted indicates that wastes would be expected to freeze in the range of 0° to -3°C depending on the concentration of dissolved solids in the occluded liquor. Little, if any additional liquor would be expected to be released from wastes after a single freeze/thaw cycle beyond that released from wastes not undergoing freeze/thaw. Therefore, for waste disposal operations which occur during winter months, exposure of wastes during transportation and handling operations to temperatures below 0°C would probably freeze the surface and eventually solidify the entire waste mass. However, this should not create drainage problems during transport and handling operations. Only where waste is densely packed or very wet could there be problems related to handling and workability of the waste with standard transport and earth-moving equipment. During cold weather (i.e., below freezing conditions) the waste should be stockpiled and transported in a relatively loose condition to ensure ease of discharge from transport vehicles and workability during placement. In some cases it may be necessary to use specially designed haulage vehicles to prevent the waste from freezing (e.g., dump trucks with sides heated by the truck exhaust).

(2) Effects on Stabilized Wastes

Freeze/thaw effects on various mixtures of fly ash and FGD waste produced from direct lime scrubbing (using carbide lime) with and without the addition of lime were studied by the University of Louisville. Six different mixtures were tested in the laboratory, five with 1:1 fly ash to FGD ratios (one without fly ash) containing 3 wt % or 5 wt %, lime added as carbide lime or CaO. The samples were cured for seven days in a humid atmosphere at room temperature and then subjected to four freeze/thaw cycles (-10°C for 24 hours followed by 20°C for 24 hours). The ASTM D560 Method for Freezing and Thawing Tests of Compacted Soil Cement Mixtures was used (except for the number of cycles).

Qualitative information was gained from the testing, although quantitative evaluations were not possible due to severe cracking during freezing and soft consistency during thawing. (It should be noted that very few soils presently used as landfill material would meet the requirements of ASTM test D560.)

TABLE III-4

SUMMARY OF FREEZE/THAW DEWATERING EXPERIMENTS

			% Solids		
	Sample Code	As-Received	As Received/ Suction	-24°C → 20°C/ Suction	-8°C → 20°C/ Suction
Lime, Centrifuge Cake	L1	65.7	70.6	68.4	71.1
Lime, Filter Cake	L2	55.1	58.4	71.1[a]	59.4
Limestone, Clarifier Underflow	LS1	57.8	68.5, 67.8	--	71.7
Dual Alkali Filter Cake	DA2				
Loose Packed (0.76 gm/cc)		61.9	64.10	63.9	63.7
Hard Packed (1.4 gm/cc)		61.9	64.10	--	63.3
Water Added (3 gm H_2O + 30 gm sludge)		59.0	64.10	--	71.8

		Amount of Liquid Extracted (gm) from 15 gm Sample[3]		
		As Received/ Suction	-24°C → 20°C/ Suction	-8°C → 20°C/ Suction
Lime, Centrifuge Cake	L1	0.6	--	0.5
Lime, Filter Cake	L2	0.7	0.65	0.6
Limestone, Clarifier Underflow	LS1	1.7	1.45	1.45
Dual Alkali Filter Cake	DA2			
Loose packed		None	--	None
Hard Packed		None	None	None
Water Added		1.5 (calculated based on added amount and result for above)	--	1.75

a) Does not include amount of water retained by filter paper. Average value calculated 0.33 g.

Source: Arthur D. Little, Inc.

In general, all samples expanded during freezing and contracted during thawing; all increased slightly in moisture content. Those which exhibited the most severe cracking also showed the greatest increases in moisture content.

Pilot-scale field studies of stabilized waste disposal were performed in above-ground pools and in pits at Louisville Gas and Electric Company's Cane Run Station using waste mixes similar to those of the laboratory tests. Many of the impoundment areas were filled during freezing conditions. There is evidence that in some cases freezing may have caused dewatering of wastes to some extent (after subsequent thawing), but freezing also produced layering in waste deposits. Frozen zones that formed on the surface of waste deposits remained frozen for four to five months when more waste was added over the surface of the fills. Further, stabilization of FGC waste with additives was impaired by freezing. In some deposits, anticipated pozzolanic reactions were delayed; in others such reactions never occurred. In one particular instance, a mixture of carbide lime FGD waste, fly ash, and carbide lime (1:1:0.03 weight proportions) emerged from a mixing truck as spheres 2.5 to 15 centimeters (1 to 6 inches) in diameter. These balls froze to rock-like hardness within hours after placement and remained rock-like for more than three months. With the advent of warmer weather, the balls thawed, dried, and in many cases crumbled.

Radian studied the effects of freeze/thaw cycles on the stability of FGC wastes as a part of a laboratory program for EPRI (8). Twenty-two different mixes of fly ash, synthetic FGC wastes, and lime were subjected to five freeze/thaw cycles. The samples were first allowed to cure under normal conditions (24°C) for 14 days prior to a ten-day period of freeze/thaw cycling. Each cycle consisted of one day at freezing conditions (-15°C) followed by one day of thawing (24°C). A set of control samples for each mix was maintained under normal curing conditions for the full 28 days.

Surprisingly, slightly higher strengths on the average were observed with the samples subjected to freeze/thaw cycles. In general, the increase in strength tended to vary with the type of ash used. For the three ashes the average increases in strength were 9%, 12%, and 27%.

It would have been expected that freeze/thaw cycling would have decreased strength due to lower rates of pozzolanic reactions and/or disruption of the internal structure of the waste mass resulting from expansion/contraction during freeze/thaw. However, Dravo has indicated similar effects of freeze/thaw on waste stabilized by its patented Calcilox® process. Freezing conditions slowed the curing process, but return to normal conditions allowed continuation of the stabilization without deleterious effects on the final strength achieved (24).

The results of the Radian study appear to contradict the field testing performed at Cane Run Station. However, an important difference in the two studies is that in the Radian work the samples were allowed to cure for two weeks prior to freeze/thaw cycling, while the materials tested at

Cane Run were subjected to freezing conditions almost immediately after mixing. The manner in which stabilized wastes are handled and placed during freezing conditions may be significant in determining the final strength achievable.

The potential effects of freezing and the possible need for slightly longer stockpile times prior to placement has been noted by IUCS (25). There has been only limited field experience with landfill-type disposal of stabilized wastes during winter freezing conditions. However, based upon laboratory work and some field experience, IUCS feels that it could be necessary to allow a few days longer stockpile time after mixing of the FGD wastes with lime and fly ash during freezing conditions to allow initiation of stabilization reactions prior to placement.

c. Fugitive Emissions

Fugitive emissions which result from essentially uncontrolled nonpoint sources (versus controlled point sources such as stacks or vents) are very difficult to monitor. No definitive research had been done to develop fugitive emissions factors for various types of FGC wastes as influenced by moisture content, age, manner of storage, and meteorological conditions (wind, temperature, etc.).

In addition to the lack of data available to quantify the emission potential, therewere also no data relating FGC waste emissions to health effects; however, general considerations may provide some perspective. At normal wind velocities, inorganic particles having diameters larger than 75 microns, No. 200 mesh, tend to settle out of the air in less than 30 meters. Generally, particles with diameters less than 30 microns have drift potentials in excess of 300 meters (26).

Particles in the 15 to 25 micron size range tend to be filtered in the nasal passages or removed at the back of the throat. Particles sizing less than 2 microns have been referenced as being a potential health hazard because they can reach the lungs and cause an irritation possibly leading to a form of pneumoconiosis. And particles less than 0.3 microns tend to "behave as part of the transporting gas, and the chances of their being centrifuged out against the walls of the respiratory track or impinged in the alveoli are virtually nil" (27).

Potential for fugitive emissions from waste disposal operations will depend importantly on a number of factors:

- characteristics of the waste--particularly particle size distribution, moisture content, and presence of fixatives which promote hardening of the waste;
- climatic conditions--evaporation and rainfall, and wind; and
- disposal operations--methods of stockpiling, handling, and placing the wastes.

Based upon available particle size distribution data, wastes produced by FGD systems are generally fine grained (less than 75 microns). Pure sulfate wastes tend to be fine sand size, while sulfite and mixed sulfite/sulfate wastes tend to be silt size. Therefore, depending on the oxidation achieved in the FGD system, the portion of particle sizes below 74 microns can range from approximately 60% to 95% (1). The fraction of the waste with particle sizes less than 2 microns is usually on the order of 5% or less (21). As a result, it is expected that of the majority of a dry waste which could be wind-blown as individual particles, only a minor portion would be susceptible to human inhalation and retention.

When fine grained particles are moist, they stick together. Most particles stick together if the moisture level is 5% or more of the wet weight and are no longer considered to be a major emissions problem (28). Dewatered wastes from FGD systems usually contain 15 wt % to 50 wt % moisture after filtration or centrifugation. Silt sized sulfite-rich wastes (which tend to be more difficult to dewater than fine sand-sized sulfate-rich wastes) can be dewatered by filtration to 35-50 wt % moisture; fine sand-sized sulfate wastes can be dewatered to as low as 15 wt % moisture (21). Therefore, despite the dewatering process the waste still contains a substantial amount of moisture.

Mine disposal of dewatered FGD wastes would include storage, handling, and transport operations, all with a potential for fugitive emissions. Drying and wind erosion of waste can also occur during exposure after placement. The extent of actual emission will depend on whether the waste surface is allowed to dry (more than 95% solids), whether crusting of the waste occurs, and whether the wind velocity is sufficient to erode and transport the particles (generally more than 10-15 mph) (26).

Fugitive emission factors are derived from wind tunnel experiments and in-field air quality monitoring around nonpoint sources. Such research was beyond the scope of this study. However, single observation tests were conducted with small samples of FGD wastes. Both sulfate-rich and sulfite-rich wastes were examined. Initially, the wastes were wet (moisture about 50% of the wet weight). The samples were allowed to dry indoors at room temperature. The samples were completely dry in one day. The dry samples were in the form of aggregate, with a crusty surface; however, the bonding between particles was weak, and a slight disturbance or wind resulted in a small cloud of dust. In actual field performance the drying rate has not been observed to be as rapid (due to factors such as rainfall, wind velocity, cloud cover, and temperature variations). Observation of piles of sulfite-rich and sulfate-rich untreated wastes produced at Gulf Power Company's Scholz Steam Plant showed little evidence of wind erosion and/or significant fugitive emissions. In fact, as the piles aged, a crust formed, tending to minimize additional drying of the piles.

A study of waste erosion potential performed by Radian (29) using small plots of a number of different types of FGD wastes confirmed this crusting phenomenon. The surface crust developed during wet/dry cycles, providing a protection coating during wind erosion experiments.

The results of these experiments and the limited field experience are not conclusive. Wind erosion during storage, handling and transport and following placement is still a potential problem.

Methods for mitigating fugitive emissions include surface moisture content and waste stabilization.

Moisture content plays an important part in fugitive emissions, so pollution may be lessened by controlling moisture. During stockpiling or transport, the waste could be sprayed with a fine water mist. Alternatively, operations may be scheduled so that the waste surface is continuously renewed by either adding moist fresh waste or removing dry exposed waste if surface crusting does not occur.

Particle size also plays an important role in fugitive emissions, so chemical stabilization of FGD waste may be used to aggregate particles. Stabilization techniques which result in a soil-like product have shown only slight effect on the particle size distribution and would likely have little beneficial impact on fugitive emissions. However, stabilization techniques which create FGD waste products resembling a soil-cement or low strength concrete offer potential as mitigative measures. For long-term exposure, stabilization techniques may only decrease the rate of fugitive emissions. Durability tests by the U.S. Army Waterways Experiment Station (30) resulted in most of the stabilized FGD wastes (except those made into a moderate strength, concrete-like material) failing the freeze/thaw exposures within a few cycles (where one cycle is designed to simulate an exposure to the elements of one year). Similarly, most of the stabilized wastes tested failed the wet/dry exposures within ten cycles. Performance failure of the samples occurred when a limited number of cycles caused disintegration. Actual data correlating laboratory testing with field performances apparently has yet to be obtained. However, long-term exposure leading to fugitive emissions from mine disposal operations is highly unlikely.

2. Chemical Impacts

a. TOS Dissolution

(1) Introduction

The leaching of sulfite (or total oxidizable sulfur - TOS) from FGC waste is of concern for two reasons. First, sulfite is readily oxidized to sulfate and can therefore deplete oxygen levels in groundwaters and in immediate dilution zones of receiving surface waters. The chemical oxygen demand (COD) of sulfite on a weight basis is theoretically equivalent to 20% of the soluble sulfite present, as shown in the following reaction equation:

$$SO_3^{=} + 1/2\ O_2 \rightarrow SO_4^{=}$$

$$(MW = 80) + (MW = 16) \rightarrow (MW = 96)$$

Second, sulfite (or TOS) is potentially toxic to exposed organisms.

Sulfite can be present in the waste in two forms: as soluble sulfite (or bisulfite) in the liquor occluded with the waste and in the solids phase as calcium (and magnesium) sulfite. Sulfite levels in the liquor phase of FGC waste can range from nil to a few thousand ppm, and the amount of sulfite in the waste can vary from nil to greater than 95% of the total calcium-sulfur salts present.

The level of sulfite will depend primarily upon the degree of oxidation in the scrubber system. The principal factors affecting oxidation are the type of FGC process in which the waste is produced, the operating conditions of both the FGC process and the boiler, and the characteristics of the coal fired. The manner in which the waste is processed (e.g., further dewatered, admixed with ash, etc.) and handled prior to and during disposal can also significantly affect sulfite levels because of sulfite oxidation by the air.

The release of sulfite from wastes due to leaching by groundwaters involves two mechanisms. The first is the displacement by groundwater flushing and/or release during consolidation of the scrubber liquor occluded with the waste. The second mechanism of sulfite release is dissolution of calcium (or magnesium) sulfite solids. The amount of sulfite released by both of these mechanisms is importantly dependent upon the permeability of the waste deposit and the hydraulic head.

In the absence of oxidation, the concentration of sulfite (TOS) in the initial flush of leachate would be expected to be identical to that in the liquor phase. Most of the liquor would be washed from the waste in the first three pore volume displacements, and concentrations of sulfite in the leachate would be predominantly due to sulfite in the liquor phase. Thereafter, the presence of sulfite in the leachate will depend primarily upon dissolution of solids. Since permeation of groundwater through the waste would normally be much slower than the dissolution rate(s) of the solids, the leachate would be expected to be saturated or nearly saturated with respect to calcium sulfite. Saturation would be dictated by the solubility product of calcium sulfite and the composition of the groundwater.

The solubility product, K_{sp}, defines the concentration of soluble species in equilibrium with a given solid phase. For calcium sulfite the solubility product can be expressed as follows:

$$K_{sp}(CaSO_3 \cdot X\ H_2O) = a_{Ca^{++}} a_{SO_3} a^{X}_{H_2O}$$

$$\simeq (\gamma_{Ca^{++},\ SO_3^{=}})^2\ m_{Ca^{++}} m_{SO_3^{=}}$$

where $\gamma_{Ca^{++},\ SO_3^{=}}$ = mean molal activity coefficient for Ca^{++} and $SO_3^{=}$

m = molal concentration of species.

Since activity coefficients vary with temperature and ionic strength, the solubility product expression can be rewritten as:

$$m_{SO_3^{=}} = \frac{K_{sp}}{m_{Ca^{++}}\ \gamma^2_{Ca^{++},\ SO_3^{=}}} = \frac{K'_{sp}(f,\mu)}{m_{Ca^{++}}}$$

Thus, for a given temperature and groundwater ionic strength the equilibrium (saturation) sulfite concentrations should be inversely proportional to the calcium concentration in the leachate.

This is a rather simplistic view of the leaching process. In reality, there will be a number of factors in addition to the groundwater temperature, ionic strength, and calcium concentration that can affect the amount of calcium sulfite that dissolves and the concentrations of sulfite (or TOS) achieved. Important among these are:

- Relative amounts of sulfite and sulfate solids in the waste and the crystalline morphology of the solids--The chemical nature of the waste will determine the solubility of the constituents (calcium, sulfite, and sulfate) and also the availability of the calcium-sulfur salts. Calcium sulfate (as gypsum) is one to two orders of magnitude more soluble than calcium sulfite. The amount of calcium sulfate which dissolves will generally be a function of the relative saturation of the groundwater and the amount and availability of calcium sulfate in the waste solids. If an untreated waste is rich in calcium sulfate, then dissolution of calcium sulfate could significantly increase concentrations of calcium in the groundwater, thereby reducing equilibrium sulfite concentrations. The rate of calcium sulfate dissolution may also dictate the amount of calcium sulfite exposed to contact with the groundwater. On the other hand, if there is very little calcium sulfate in the waste and it exists as $CaSO_4 \cdot 1/2\ H_2O$ in solid solution with calcium sulfite, then the amount of calcium sulfate which dissolves can be limited by the overall rate of dissolution of the crystal (and the leachate may be unsaturated with respect to calcium sulfate).

In the case of stabilized wastes or wastes where pozzolanic reactions have encapsulated the calcium-sulfur salts or incorporated the calcium sulfite and sulfate in calcium aluminate complexes, not only can the availability (exposure) of the calcium-sulfur salts to dissolution be significantly reduced, but the solubility of the solids reduced appreciably. Hence, sulfite concentrations in leachate may be limited by both dissolution kinetics as well as chemical equilibrium.

- Groundwater acidity/waste alkalinity--Neutralization of groundwater acidity by residual alkalinity in the waste (e.g., $CaCO_3$, CaO, $Ca(OH)_2$, $NaOH$, Na_2CO_3) can also alter soluble calcium concentrations in the leachate, thereby affecting dissolution of calcium-sulfur salts. Depending upon the groundwater acidity composition, neutralization could result in a decrease in calcium concentration precipitation of calcium salts (e.g., calcium sulfate) or an increase due to dissolution of alkaline calcium species.

  However, if the alkalinity of the waste is considerably less than the acidity of the groundwater (or the amount of waste relative to groundwater flow is very small), then TOS levels in leachate can increase significantly. The solubility of calcium sulfite is pH sensitive at moderate pH levels. Calcium bisulfite is highly soluble and the dissociation constant for bisulfite is on the order of pK = 7 (i.e., at a pH of about 7, roughly half of the TOS will be present as bisulfite and half as sulfite). Thus, an appreciable amount of calcium sulfite can be dissolved in highly acidic groundwater. If the remaining acidity is later neutralized, then reprecipitation of calcium sulfite would be expected to occur.

- Groundwater oxygen content--The oxygen content of the groundwater would be expected to have less of an influence on soluble sulfite levels, although it could significantly affect the amount of solids dissolved. Since soluble sulfite can be readily oxidized to sulfate, any soluble sulfite from the dissolution of waste solids would be expected to be converted to sulfate with a corresponding decrease in oxygen levels in the groundwater. This dissolution and oxidation would be expected to continue until all oxygen was depleted at which point a sulfite equilibrium concentration would be established in the leachate. For example, assuming a K'_{sp} of 10^{-6} (moles^2/liter^2) for $CaSO_3 \cdot 1/2\ H_2O$ and an unsaturated groundwater containing 200 ppm of calcium and 8 ppm of oxygen, the final sulfite level would be about 15 ppm. While this would be almost the identical level to that achieved were there no oxygen initially present, the presence of oxygen would have more than doubled the quantity of waste dissolved (per unit volume of groundwater).

- Microorganism activity--The activity of microorganisms in the groundwater can complicate these simple chemical reactions. Microorganisms can catalyze chemical reactions and affect the local sulfur balance (via oxidation/reduction mechanisms). For example, microbial activity could reduce sulfate and sulfite, resulting in evolution of H_2S or SO_2. Because of the wide variations in waste compositions (including trace contaminants) and disposal environments, such biochemical effects do not readily lend themselves to generalization.

(2) Published Studies

Laboratory Investigations

There have been only a few studies to date which have addressed the question of calcium sulfite dissolution and sulfite leaching from FGC wastes. What data are available, though, do indicate that sulfite levels in leachates can vary greatly depending upon the FGC system, the condition of the waste, and the manner in which the leachate tests are run.

The most comprehensive published data on sulfite levels in waste leachates were available from accelerated laboratory leaching tests performed by Aerospace under contract to the EPA (9, 31). In this work, the leaching behavior of more than half-a-dozen wastes from different FGC systems was evaluated. Tests were run on stabilized and unstabilized wastes under both aerobic and anaerobic conditions using unbuffered leaching water with pH's ranging from 4 to 9 (adjusted by addition of HCl or NaOH). Sulfite concentrations in leachates have been reported for five different untreated wastes (four sulfite-rich and one sulfate-rich) and four stabilized wastes. The sulfate-rich waste ($CaSO_4/CaSO_3 > 0.9$), which had an initial sulfite concentration in the waste liquor of less than 1 ppm, produced sulfite concentrations in leachate samples consistently less than 1 ppm. For the sulfite-rich wastes, sulfite concentrations in the waste liquors ranged from approximately 1 ppm to as high as 140 ppm, and concentrations of sulfite in the first pore volume displacements under aerobic conditions ranged from 18 to 48 ppm. Relatively stable concentrations of most species were reached after the first few pore volume displacements with TDS levels ranging from 1600 to 2400 ppm and soluble sulfite concentrations of 9 to 30 ppm for the different wastes. However, the leachate data do not include analyses for calcium, magnesium, and sodium, which would allow the determination of calcium sulfite solubility products and possibly an analysis of the effects of waste characteristics on the levels of sulfite achieved.

The effects of waste stabilization on the levels of sulfite in leachates are not well defined, although there are significant data trends. In the Aerospace work, leachate data are available under both aerobic and anaerobic conditions for wastes treated by the Chemfix, IUCS (Poz-O-Tec®), and Dravo

(Calcilox®) processes. In general, sulfite levels under anaerobic leaching conditions were greater than levels achieved under aerobic leaching conditions for equivalent pore volume displacements. The differences ranged from 1 or 2 ppm to as much as 30-35 ppm. Also, sulfite levels in anaerobic leaching tests with stabilized materials tended to be slightly greater than sulfite concentrations in leaching tests with untreated materials under aerobic conditions, even though both sulfate levels and TDS stabilized waste leachates were substantially lower than the leachates from untreated materials. This could be explained by oxidation of sulfite to sulfate.

Field Observations

Additional data on sulfite leaching are available from the dual alkali prototype test program conducted at Gulf Power Company's Scholz Steam Plant in Sneads, Florida (17). The program jointly funded by The Southern Company Services, the Gulf Power Company, EPA, and EPRI included monitoring of leachate from the waste disposal impoundment. The untreated sulfite-rich waste filter cake (50-60% solids) was dumped in a 3/4-acre lined pit equipped with a trench underdrain system to collect leachate. The wastes were not compacted and no attempt was made to divert or minimize rainwater infiltration.

Underdrainage from the pit was sampled monthly for a year during disposal and for six months following completion of the operation. A significant quantity of the filter cake placed in the pit was unwashed or poorly washed so that the liquor phase contained appreciable concentrations of sodium sulfite and sulfate, which would not be characteristic of filter cake from full-scale systems. Consequently, total dissolved solids concentrations were relatively high, typically between 10,000 and 20,000 ppm. TOS concentrations varied from as low as 54 ppm to as high as 500 ppm and typically ran 100-250 ppm, while calcium levels ranged from 210 to 420 ppm. All samples were highly alkaline (pH's = 11-12.4), and all but two contained relatively low levels of dissolved oxygen (do = 3.4-6.1 ppm). Based upon rainfall (and evaporation) data for the period and estimates of the quantity of waste placed in the pit, the amount of water estimated to have infiltrated the waste over the 18 months of sampling corresponded to roughly one pore volume displacement (or less). Thus, the concentrations measured in the leachate would be expected to be representative of a first flush liquor. This is consistent with the leachate data, which showed no significant trends (decrease or increase) in TDS or major species concentrations over the 18 months.

Analysis of the leachate compositions indicates that some of the calcium sulfur solids dissolved in the mixed rainwater/occluded liquor and that some of the sulfite present in the leachate oxidized prior to and after sampling. Therefore, the concentrations of sulfite in the leachate, while higher than equilibrium levels expected from dissolution of calcium sulfite alone, were lower than the sulfite concentration in the liquor originally occluded in the filter cake.

(3) Laboratory Equilibrium Tests

Because of the lack of definitive data on the dissolution potential of sulfite from sulfite-rich FGC wastes, laboratory testing was performed as a part of this study to better quantify the solubility of calcium sulfite in different types of FGC wastes. The experiments were conducted to determine the equilibrium solubility of TOS in simulated groundwater environments, focusing on the effects of variations in concentrations of species expected to have the largest impacts on calcium sulfite solubility. The factors studied were those which could affect the activities of calcium and sulfite ions, i.e., total ion concentration (ionic strength), and variations in principal waste or groundwater constituents which can act as complexing agents or form in pairs.

No attempt was made to study the effects of microorganisms or to cover the wide range of possible groundwater (or mine water) concentrations. It is recognized that the fate of sulfite in the wastes will depend importantly upon the characteristics of the groundwater contacting the wastes; however, an investigation of the full range of compositions and conditions is beyond the scope of this study.

Six experiments were carried out in synthetic groundwaters using two different unstabilized, sulfite-rich FGD wastes (without fly ash). The tests were run under anaerobic conditions (nitrogen purged) with neutral groundwater. This resulted in leachates (elutriates) that were basic (pH $\geq$8.0). Acidic conditions were not tested, since these would represent worst case conditions and the results would not provide a good indication of the minimum sulfite dissolution potential. For the same reason the ionic strengths of the synthetic groundwaters were maintained at or below about 0.02 M.

Table III-5 summarizes the chemical properties of the sulfite-rich waste samples used. In both samples, $CaSO_3 \cdot 1/2\ H_2O$ accounted for about 75% of the total solids present. The dual alkali sample had more dissolved solids in the occluded liquor than the direct lime sample. Although complete liquor analyses were not performed, the ionic strength of the liquor occluded in the dual alkali waste is believed to have been two to three times higher than that of liquor in the direct lime waste.

The dual alkali waste was prewashed with distilled water to remove most of the soluble solids in the occluded liquor prior to testing. Slurries containing 0.5 wt % solids were then prepared with the test solutions (synthetic groundwaters). The slurries were agitated under a nitrogen purge and samples taken at one, two, and three hours were analyzed to ensure that equilibrium had been achieved. There were no significant differences in the compositions of the one-, two-, and three-hour samples, indicating that equilibrium was reached in less than one hour.

Table III-6 summarizes the initial test solution conditions and final elutriate concentrations for the species of interest. The results indicate

TABLE III-5

SUMMARY OF WASTE SAMPLES TESTED

Sample Designation	DA2	L2
Type of System	Dual Alkali	Direct Lime
Weight % Solids	63	52
Analyses of Total Solids		
Ca (mmols/dry gm)	---	7.2
TOS (mmols/dry gm)	5.9	5.8
Wt % Acid Insolubles	Nil	1.0
Analysis of Occluded Liquor		
Ca^{++} (M)	0.022	0.019
$SO_3^{=}$ (M)	0.0031	0.0022
Apparent K_{sp} $CaSO_3$ (M^2)	6.8×10^{-5}	4.2×10^{-5}

Source: Arthur D. Little, Inc.

TABLE III-6

SOLUBILITY OF $CaSO_3$ IN SYNTHETIC MINE WATERS

Experiment and Number	Type of Waste	Initial Conditions[a,b]		Ionic Strength (M)	Equilibrium Conditions				Ionic Strength (M)	Apparent K_{sp} (M^2) $[Ca^{2+}] \times [SO_3^=]$
		Ca^{2+} (ppm)	Mg^{2+} (ppm)		Ca^{2+} (ppm)	Mg^{2+} (ppm)	pH	$SO_3^=$ ($M \times 10^4$)		
1 (Base)	Prewashed DA2	6	2.2	0.0014	115	0.1	11.20	3.8	0.011	1.0×10^{-6}
2 (μ Effect)	Prewashed DA2	6	2.2	0.0214[c]	121	0.5	11.23	9.0	0.032	2.7×10^{-6}
3 (Ca Effect)	Prewashed DA2	234[d]	2.7	0.0172	342	0.4	---	3.8	0.028	3.2×10^{-6}
4 (Waste Effect)	L2	234[d]	2.7	0.0172	318	3.0	8.0	4.2	0.027	3.3×10^{-6}
5 (Mg Effect)	Prewashed DA2	8	34[e]	0.0099[f]	204	0.1	---	6.0	0.023	3.1×10^{-6}
6 (SO_4 Effect)	Prewashed DA2	12	2.0	0.0107[f]	150	0.4	---	8.0	0.024	3.0×10^{-6}

---

a. All solutions contain 11 ppm Na^+, 59 ppm HCO_3^- at initial pH = 7.

b. Concentrations derived from data in Geological Survey Water - Supply Paper 1473, Study and Interpretation of the Chemical Characteristics of Natural Water by John D. Hem.

c. Added as 0.02 M $NaClO_4$.

d. Added as $Ca(ClO_4)_2$.

e. Added as $Mg(ClO_4)_2$.

f. Also contains $NaClO_4$.

g. Added 300 ppm $SO_4^=$ as Na_2SO_4.

Source: Arthur D. Little, Inc.

increases of 80 to 200 ppm (2 to 5 x 10^{-3} M) calcium due to dissolution of the solids (the contribution from dissolved calcium in the liquor phase would have amounted to less than 2 ppm). Increases in sulfite concentration ranged from 30 to 72 ppm (3.8 to 9.0 x 10^{-4} M).

The larger increases in calcium concentration reflect dissolution of other calcium solids in the wastes--principally $CaSO_4$ but also $Ca(OH)_2$ in the case of the dual alkali waste. The dissolution of $Ca(OH)_2$ (as well as release of residual NaOH occluded in the waste) from the dual alkali waste is evident from the high pH's of the dual alkali elutriates (Experiments 1-3,5,6). These high pH's resulted in precipitation of magnesium as $Mg(OH)_2$ ("K_{sp}" $\approx 10^{-11}$). No precipitation of magnesium was observed with the direct lime waste (Experiment 4). The direct lime waste had low residual alkalinity, and consequently there was little increase in the pH of the simulated groundwater.

The results show that under neutral to basic groundwater conditions the most important factors governing the dissolution of sulfite from sulfite-rich wastes are ionic strength and the hardness of the groundwater. For a soft groundwater, increasing the ionic strength of the elutriate by threefold (Experiments 1 and 2) increased the equilibrium sulfite concentration and apparent "K_{sp}" by about a factor of 2.5. Increasing the groundwater hardness under conditions of similar ionic strength (Experiments 2 and 3) reduced significantly the amount of sulfite dissolved but did not appreciably affect the apparent solubility product. The data do suggest a slight effect of calcium concentration on the apparent solubility product. The trend in the data from Experiments 2 through 6 is an increase in the solubility product with increasing calcium concentration. A possible explanation is the presence of calcium sulfite ion pairs in solution. However, the effect is small and could easily be attributed to experimental error in the calcium and sulfite analyses.

There appears to be little effect of waste source (Experiments 3 and 4) on the solubility product, and the effect of sulfate concentration is apparently simply one of changing ionic strength. No effect of magnesium complexing on the solubility product or sulfite dissolution could be assessed using the dual alkali waste (Experiment 5) due to precipitation of the magnesium at the high elutriate pH.

The importance of dissolved solids concentration on sulfite dissolution is shown in the plot of the apparent solubility product of calcium sulfite versus ionic strength presented in Figure III-1. Data Curve No. 1 incorporates the data from these experiments along with results available from other laboratory experimentation performed as a part of related FGD scrubber studies. Included are data from studies conducted by Arthur D. Little, Inc. and EPA in the evaluation of dual alkali technologies (19) and additional work under this program from the assessment of ocean disposal alternatives.

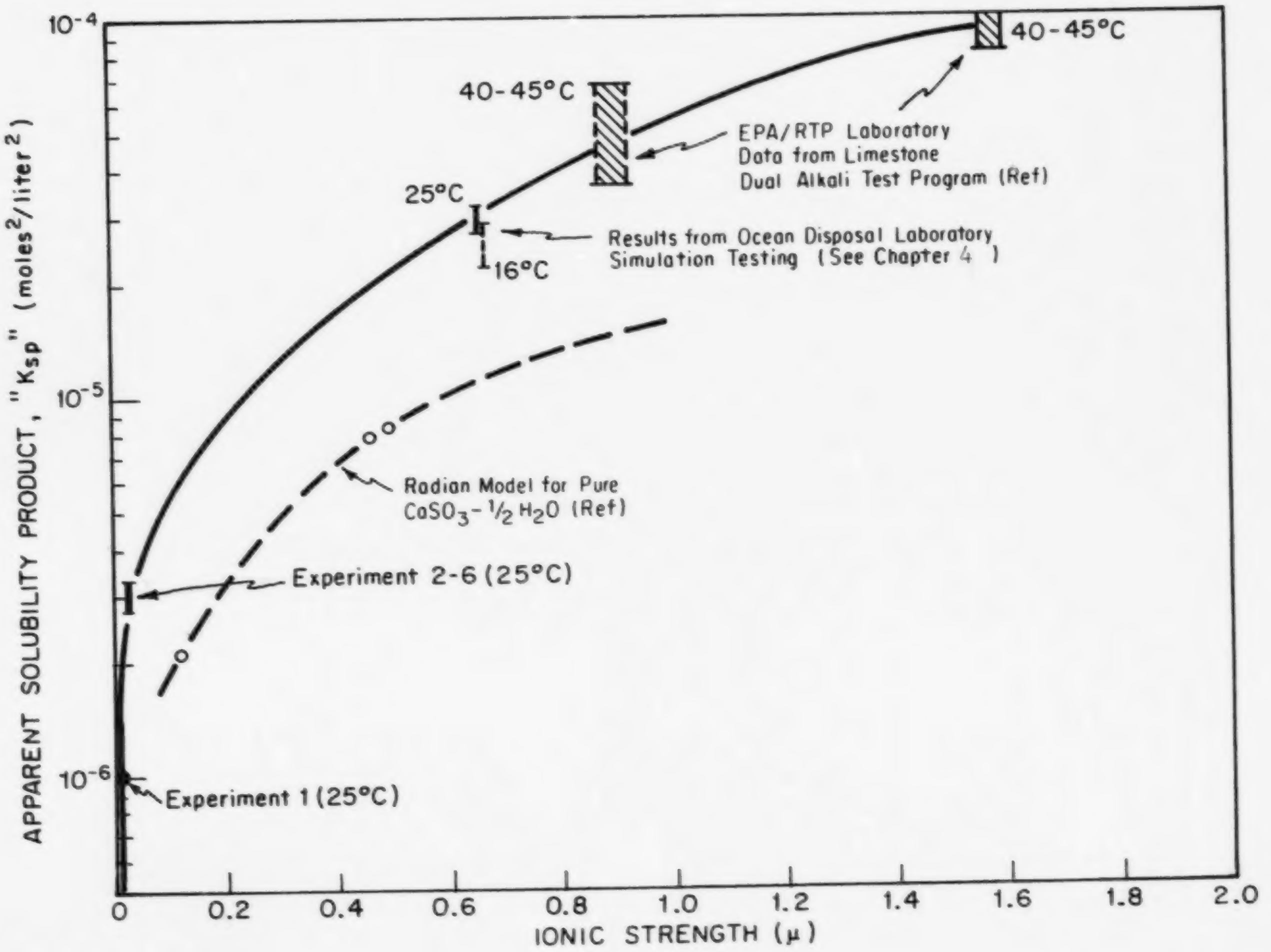

FIGURE III-1 APPARENT SOLUBILITY PRODUCT OF $CaSO_3$ vs. IONIC STRENGTH OF SOLUTION

Source: Arthur D. Little, Inc.

These data cover a range of temperatures from 16°C (in the ocean simulation testing) to about 45°C (in the dual alkali technology work). There is a slight influence of temperature on calcium sulfite solubility as indicated in the ocean experiments. However, the effect of temperature is relatively small over this range when compared with ionic strength.

Also shown in Figure III-1 as Curve No. 2 are data published by Radian Corporation (32). These data were used by Radian to develop a model of calcium sulfite solubility in scrubber liquors. The apparent calcium sulfite solubility products calculated from the Radian experimental data and from the Radian model are a factor of 3 to 5 lower than the other laboratory data presented in Curve No. 1. This discrepancy could be due to the purity of the calcium sulfite solids used in the different studies.

The empirical solubility product/ionic strength relationship of Curve No. 1 indicates that sulfite equilibrium concentrations in leachates from untreated sulfite-rich wastes could range from tens to hundreds of ppm depending upon groundwater ionic strength and calcium concentration, and waste properties. In soft groundwater containing low levels of TDS under neutral to basic conditions, sulfite ion concentrations would be expected to be less than 50 ppm. In groundwaters containing high TDS levels, potential sulfite ion concentrations could be 300-400 ppm or higher, although the competing effects of ionic strength and calcium concentration (for hard water) could limit sulfite concentrations to less than 100 ppm.

These estimates do not, of course, take into account the effects of microorganisms, oxygen content of the groundwater and channeling/cross-mixing of groundwater flow through the waste deposit. Of perhaps greater impact, it does not take into consideration acidic groundwater conditions which could dissolve significantly more waste and sulfite.

b. Offgassing Potential

The disposal of FGC wastes, particularly sulfite-rich materials, offers potential for production and release of gases--notably CO_2, H_2S, and SO_2. Important factors expected to govern the generation of such gases are:

- Waste composition--moisture content, sulfite- versus sulfate-rich, presence of unreacted $CaCO_3$ and/or other alkali value ($Ca(OH)_2$) which can neutralize acidic conditions, nutrient content, etc.;

- Waste processing--stabilization of the waste to minimize permeability and reactivity; and

- Disposal environment--quantity and composition of groundwater contacting the waste, presence of soil and its nutrient content, presence of microbial activity that can be supported by the waste or local soils.

Of principal concern is the release of H_2S and SO_2 because of their environmental impact potential. H_2S may be generated in anaerobic environments by sulfate (sulfite) reducing microorganisms. SO_2 could be produced by contact of sulfite-rich wastes with acidic groundwaters. Either of these conditions could conceivably exist in mine disposal operations.

Laboratory studies have been undertaken to investigate the potential for production of these gases. Work on SO_2 offgassing has been performed by Arthur D. Little as a part of this program. Work on H_2S production was conducted by Radian under a program funded by EPRI (33).

(1) SO_2 Offgassing

When sulfite-containing FGC wastes are exposed in a mine environment containing acid mine drainage, it is possible that the calcium sulfite portion of the waste will react with sulfuric acid present in the drainage, resulting in dissolution of calcium sulfite and release of SO_2 gas. This reaction would be most likely to occur during the initial periods of waste disposal, particularly in underground mines where the relative amounts of mine water to waste in the void could be high and any buffering capacity or alkalinity in the waste may be insufficient to neutralize the water acidity. Continued disposal of waste may reduce or eliminate the formation of acid drainage by filling the voids, eliminating air and reducing oxidation of coal and the flow of water.

For waste disposed in worked-out portions of active underground mines the evolution of SO_2 could be hazardous to personnel in the vicinity of the disposal operation. Waste disposed in abandoned mines having pools of acid drainage could generate pockets of SO_2 gas which may eventually release to the atmosphere or nearby mines. Immediate release of gas through boreholes used for disposal of slurries is also possible.

The release of SO_2 can be described by the following equations:

$$2CaSO_3(s) + H_2SO_4 \rightarrow 2Ca^{++} + 2HSO_3^- + SO_4^=$$

$$2Ca^{++} + 2SO_4^= + 4H_2O \rightarrow 2CaSO_4 \cdot 2H_2O(s)$$

$$\underline{2HSO_3^- + H_2SO_4 \rightarrow 2H_2O + 2SO_2\uparrow + SO_4^=}$$

$$CaSO_3^- + H_2SO_4 + 2H_2O \rightarrow CaSO_4 \cdot 2H_2O + H_2O + SO_2\uparrow$$

The amount of SO_2 evolved would depend upon several factors:

- sulfite content of the waste;
- acidity of the water;
- alkalinity of the waste;

- relative amounts of water and waste; and

- degree of mixing or contact of the waste and groundwater--i.e., manner of disposal, physical form of the waste (slurry, soil-like solid, stabilized form, etc.)

In order to investigate the potential for SO_2 release, a series of experiments were performed using simulated acid mine water and samples of two sulfite-rich wastes from operating FGD systems. Of the four general categories of acid mine drainage shown below, Class I was selected for testing.

Category	pH	Acidity (mg/ℓ of $CaCO_3$ equiv.)	Fe^{+2} (mg/ℓ)
Class I	<2-4.5	1,000 - 15,000+	500 - 10,000+
Class II	3.6-6.6	0 - 1,000	0 - 5,000
Class III	6.5-6.8	0	0
Class IV	6.5-8.5	0	50

Clearly, little or no offgassing of SO_2 would be expected for Class III and IV waters because at the pH levels indicated (pH > 6.5) there would be little dissolution of $CaSO_3$ and the partial pressure of SO_2 over the liquor would be small. The maximum potential for SO_2 release would occur in Class I waters with acidity levels equivalent to as high as 15,000 mg per liter of $CaCO_3$ (i.e., $\sim$0.3 M acidity as H^+).

The experimental matrix was designed to examine the following effects:

- water acidity (pH = 2-3.6);

- initial and final pH of mix;

- degree of agitation;

- reaction time; and

- surface area and solids/water ratio.

The experiments were batch tests involving mixing simulated acid water with prewashed sulfite-rich FGD wastes to produce slurries of varying solids levels. The two wastes used were filter cakes from dual alkali (DA2) and direct lime scrubber systems (L2). The composition of these samples was provided in Table III-2. The wastes were prewashed to remove most of the occluded liquor in order to focus on the impact of $CaSO_3$ dissolution.

Two sets of runs were made. The first consisted of one-step dissolution/offgassing runs in which slurries were prepared and the amount of SO_2 offgassed measured after 25 to 40 minutes of reaction. Most of these runs were made using dual alkali waste at slurry levels ranging from 0.05 to 0.25 wt % solids. Some of the tests were performed with continuous agitation, others with no agitation. In the latter case the slurries were initially stirred for two seconds prior to allowing the solids to settle in order to ensure a homogeneous slurry for sampling.

Experimental conditions and results for this first set of runs are given in Table III-7. The results clearly show the importance of pH on SO_2 release. As expected, the lower the pH (more acid than water), the greater the SO_2 evolution. With low acidity water ($pH > 3$) there was little or no SO_2 produced, while with the highly acidic water ($pH \simeq 2$) as much as 0.2 ml of SO_2 was produced per gram of dry solids.

However, even with the highly acidic water the manner in which the waste is contacted with the water is a significant factor in the amount of SO_2 evolved. Allowing the waste to remain relatively undisturbed in the water resulted in the generation of considerably more SO_2 than when the solids were mixed with the water (Experiments 1 and 4). Mixing the slightly alkaline waste with the acidic water increased the pH sufficiently to suppress dissolution of $CaSO_3$. When the slurry was not agitated, only a small fraction of the total alkalinity in the waste was initially exposed to the water in the vicinity of the waste. Consequently, some calcium sulfite was dissolved and SO_2 offgassed before the pH was raised sufficiently to stop dissolution.

These effects of pH and waste/water interaction are further confirmed in Experiments 2 and 3. As the initial pH of the water is lowered, more SO_2 is produced. And when a lower waste/water ratio is used, more $CaSO_3$ is dissolved and SO_2 evolved per unit of waste.

Therefore, conditions conducive to SO_2 release are:

- high water acidity;
- low waste alkalinity;
- low waste-to-water ratios; and
- poor mixing of waste and water.

The effects of pH and waste type on SO_2 production were studied further in a second set of runs in which SO_2 evolution was monitored with time as pH of the slurries increased. Three experiments were performed, one with dual alkali waste and two with direct lime scrubbing waste. In one of the experiments with the direct lime waste the sample was ground to provide roughly three times the surface area of the as-received material.

The slurries were prepared with each material (0.25 wt % for dual alkali and 0.12 wt % for direct lime), stirred for two seconds, and allowed to settle. The atmospheres above the slurries were purged periodically with nitrogen and the amount of SO_2 produced was measured.

TABLE III-7

ONE-STEP SO_2 EVOLUTION STUDIES - TOTAL RELEASE

Experiment No.	Condition/Variation	Waste	Acid Water		Wt % Slurry[b]	TOS Present (mmols added)	Reaction Conditions		Final pH	SO_2 Released		
			$[Fe^{+2}]$ (ppm)[a]	pH			Agitation	Duration		Total mℓ	mℓ/Dry gm	% of TOS
1	High Acidity - Base Run (No Stirring)	DA2	11,000	2.1	0.25	1.5	Not Stirred	30 Mins.	2.9	0.022	0.09	0.07
2	- Longer Time/Lower pH	DA2	11,000	2.0	0.25	1.5	Not Stirred	40 Mins.	2.8	0.056	0.22	0.17
3	- Less Waste	DA2	11,000	2.1	0.13	0.8	Not Stirred	30 Mins.	2.6	0.018	0.14	0.10
4	- Agitation	DA2	11,000	2.1	0.25	1.5	Stirred	30 Mins.	4.6	<0.002	<0.01	<0.01
5	Low Acidity - Base Run (No Stirring)	DA2	560	3.6	0.25	1.5	Not Stirred	45 Mins.	3.8	<0.001	<0.01	<0.01
6	- Less Waste	DA2	560	3.4	0.05	0.3	Not Stirred	25 Mins.	3.65	<0.001	0.01	∼0.01
7	- Different Waste (Stirring)	L2	560	3.7	0.05	0.3	Stirred	30 Mins.	6.2	Not Detected	--	--

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[a] Present as $Fe(SO_4)/Fe(HSO_4)_2$.

[b] % Slurry - grams dry waste/100 mℓ total liquor.

Source: Arthur D. Little, Inc.

Results of these tests are shown in Figure III-2. Most of the SO_2 released from the as-received materials is produced in the first 15 minutes. As the pH begins to approach 2.8, SO_2 production decreases to nil. Interestingly, the ground direct lime scrubbing sample produced much more SO_2 than the unground sample and continued to produce SO_2 for a longer time and at slightly higher pH's. While it is not unexpected that the ground sample could produce more SO_2 (more surface area with a low alkalinity content), the reason for the continuation of SO_2 production to higher pH's with the ground direct lime scrubbing sample (and the dual alkali sample) than with the as-received sample is not fully understood. It may be due to (partial) encapsulation of the direct lime waste particles with calcium sulfate which is relatively insoluble at pH's in the range of 2.5-3.0. Grinding the sample would expose more sulfite for dissolution. Analyses of the wastes show that the direct lime waste contains significantly more sulfate (∿20 mol % of the $CaSO_x$) than the dual alkali waste (less than 15 mol % of the $CaSO_x$).

A direct comparison between the wastes cannot be made from the results of this second set of experiments because of differences in solids concentrations used. However, the effects of differences in the wastes can be seen by comparing the results of the run using as-received lime with the results of Experiment 3 (Table III-7) using dual alkali waste. Both of these experiments were performed at about 0.12 wt % solids. The dual alkali waste produced less SO_2 in 30 minutes than was produced with direct lime waste in 3 minutes. This can be attributed to a slightly higher alkalinity with the dual alkali waste.

The overall release of SO_2 in these experiments represented only a small fraction of the sulfite available; however, the quantities of SO_2 were not insignificant. The maximum total release measured was equivalent to about 0.33% of the TOS present (∿0.5 mℓ SO_2/dry gram) with the ground direct lime scrubbing waste. With unground dual alkali and direct lime wastes, the maximum total SO_2 released was about half of this--approximately 0.17% of the TOS present (∿0.22 mℓ SO_2/dry gram of waste). These quantities correspond to about 0.5 m^3 (16 scf) of SO_2 and 0.2 m^3 (7 scf) of SO_2 per dry metric ton of waste, respectively.

Some perspective on the potential magnitude of an SO_2 offgassing problem in an active underground mine can be provided by considering the disposal of untreated sulfite-rich waste in an Eastern mine producing 500,000 tons of high sulfur (3.5% S) coal per year. Assuming all of the FGD waste produced was returned to the mine for disposal, then on the average about 8 metric tons per hour of dry FGD waste would be placed in the mine. If only .03 m^3 (1 scf) of SO_2 were released per dry metric ton of waste (∿0.02-0.03% of the TOS), then about 700 m^3/minute (25,000 scfm) of ventilation air would be required in any active mining areas near the disposal operation to ensure SO_2 of less than 5 ppm (the 8-hour average Threshold Limit Value recommended by OSHA). This would be three times the minimum of 9,000 cfm of air required by the Code of Federal Regulations, Title 30 (July 1976), for the last cross-cut, and almost ten times the minimum ventilation rate of 3,000 cfm required at the working face.

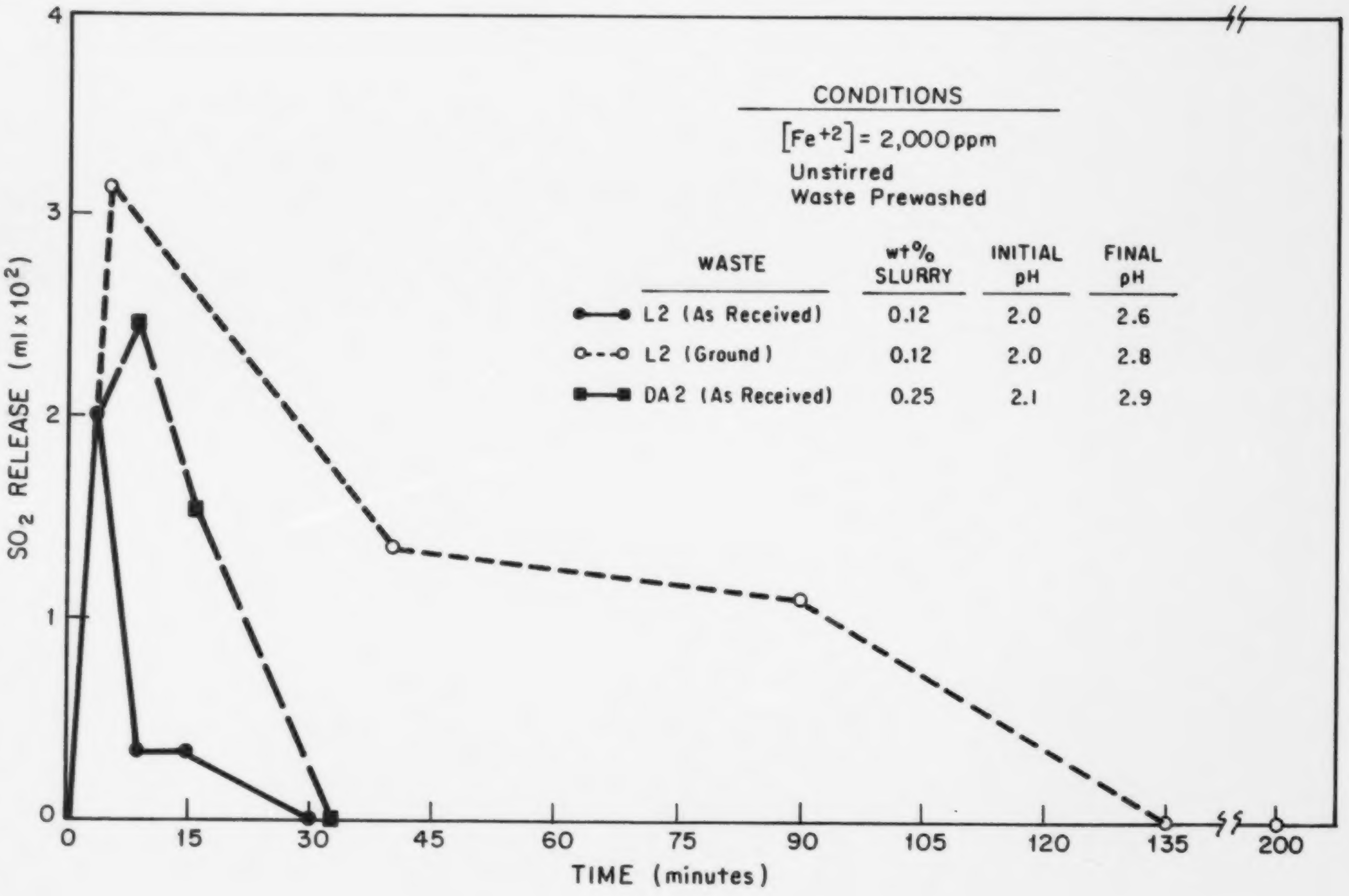

FIGURE III-2 SO_2 RELEASE FROM SOME FGC WASTES

Source: Arthur D. Little, Inc.

These experiments and the above example may be considered a worst-case scenario. The wastes were prewashed to remove the occluded liquor which certainly contained alkalinity that could have partially neutralized the acid water. Very low slurry concentrations were used, concentrations which would probably not be encountered in a mine disposal operation except possibly at the initial phase of pumping slurry into a mine void containing a pool of acid mine drainage, and highly acidic water was used in the testing.

However, the experiments do indicate there is a potential immediate impact of sudden SO_2 offgassing when a waste is contacted with highly acidic mine drainage. Certainly, if the pH of the drainage in contact with the waste is not well above 3.0, then SO_2 evolution can be expected, and it may represent not only a health problem to mine workers in active mine disposal operations but may have some localized environmental impacts as well.

There are a number of measures which can be taken to avoid the potential for immediate offgassing including:

- avoiding putting sulfite-rich wastes in mine areas exhibiting highly acidic drainage (e.g., $pH < 3.5$);
- pumping out and treatment of acid mine drainage prior to disposal of FGC wastes;
- preneutralization of acid mine drainage pools with lime or limestone slurries; or
- admixture of limestone or lime with the wastes prior to disposal.

The longer term potential for SO_2 offgassing cannot be easily predicted. The TOS dissolution studies previously discussed indicate that even under alkaline conditions, equilibrium TOS levels of tens to hundreds of ppm can be reached in water contacting sulfite-rich wastes. If the water were acidic, much higher levels could eventually be achieved. Over the long term, facultative anaerobic microorganisms could cause SO_2 evolution by catalyzing acid formation and/or reducing sulfate to sulfite and SO_2. Ferric and ferrous iron can also play a role in SO_2 offgassing. Ferric iron can oxidize sulfite to sulfate. The ratio of ferric to ferrous iron will depend upon the oxygen availability with the mines and the presence of iron-oxidizing microorganisms which catalyze the oxidation of ferrous iron to ferric.

If SO_2 were produced, it would be expected that it would eventually be released to the atmosphere through boreholes, cracks and fissures, and mine accessways. Research on gas evolution from mines (i.e., radon and carbon dioxide) has shown that mines can suddenly "belch" gas when there is a drop in barometric pressure.

Measures to prevent TOS dissolution and offgassing can be directed toward minimizing groundwater infiltration and contact (e.g., maximum filling of void areas and use of bulkheads to contain wastes in discrete areas) and, if necessary, stabilization of the waste to reduce permeability and sulfite availability.

(2) H_2S Offgassing

There have been a few instances where H_2S release from FGC wastes has been detected or noted; however, there had been little work performed to date to assess the potential for H_2S production from FGC wastes. The most prominent work in this area has been a laboratory study conducted by Radian Corporation for EPRI, published in 1979 (33). Radian investigated the release of H_2S from soil/FGC waste mixtures. Three different FGC wastes were used--sulfate-rich (synthetic), mixed sulfite/sulfate (synthetic), and sulfite-rich (direct lime scrubbing)--and two different soils--a field sample (sparsely vegetated field) and a riverbank soil. The wastes were mixed in water with roughly equal quantities of soil to produce 8% slurries and monitored for 48 days. Some samples were tested with only those indigenous sulfate-reducing bacteria (*Desulfovibrio desulfuricans*) present in the soil samples; others were inoculated with a culture of the same species.

The results of the testing indicated that this bacterium was able to reduce the FGC wastes under anaerobic conditions and a self-controlled pH of 8.3 to 8.7, resulting in the production of H_2S gas. The amount of gas produced varied with the sulfite content of the waste and the type of soil. The gypsum waste produced little more H_2S gas than the soil samples alone. The sulfite containing wastes with the riverbank soil produced the highest levels of H_2S. Without inoculation the synthetic sulfite material in 48 days released a total amount of H_2S equivalent to about 0.25 m^3 of H_2S per dry ton of FGD waste, while the direct lime scrubber system sample produced the equivalent of about 0.65 m^3 of H_2S per dry ton of waste. The final stable H_2S production rates for these samples were equivalent to about 0.005 m^3 per day per dry ton for the synthetic material about 0.01 m^3 per day per dry ton for the direct lime scrubber sample. Thus, *if* there were sufficient nutrient available, sufficient moisture, and the proper pH (6-9) to sustain the final stable H_2S production rate, then bacteria could conceivably produce on the order of 2 m^3 per year per dry metric ton of sulfite-rich waste.

How much, if any, H_2S might be generated in mine disposal environments can only be assessed on a site-specific basis. In general, the potential would appear to be greatest in surface mines where wastes were in contact or mixed with soils and in anaerobic underground mine environments.

The same measures available for minimizing SO_2 offgassing can be taken to avoid H_2S production if it is perceived to be a potential problem. These include:

- proper selection of disposal sites and disposal methods (e.g., placement of waste in the pit bottom of a surface mine versus placement in the spoil banks prior to reclamation);

- waste treatment/stabilization prior to disposal to produce a material with low permeability and lower sulfite availability; and

- maximum filling of underground mine voids and use of bulkhead containment where necessary to minimize contact with water.

c. Bulkhead Corrosion Potential

The use of bulkheads for containment of FGC wastes in underground mines may be required, particularly in active mines. Construction of such bulkheads would probably be of concrete with steel reinforcements. Because of the potential for high levels of dissolved solids (e.g., sulfate, sulfite, chloride) in FGC waste liquors and leachates, there is potential for corrosion and deterioration of concrete and steel used for waste containment. Levels of dissolved solids ranging from a few thousand to tens of thousands ppm have been measured in waste liquors. The principal species are usually calcium, sodium, magnesium, chloride, sulfate, and sulfite. Liquor pH's typically range from 6.5 to 12.0.

Corrosion of structural concrete in the presence of sulfate-containing waters and soils has been recognized at least since 1756. While the mechanism of sulfate attack is still not fully understood, the following principles seem to be fairly well established (34):

- Concrete is attacked by sulfates (and other aggressive chemicals) only in solution above some minimum concentration. Solid dry chemicals rarely, if ever, corrode concrete directly. Hence, it is the leachate from FGC wastes and the entrained liquors which are of major concern.

- A corrosive solution under pressure from one side will corrode concrete more rapidly and at lower solute concentrations than the same solution without pressure to force it into the concrete structure. Thus, still water with sulfate concentrations of 300-500 mg/ℓ may not significantly decrease concrete lifetime, while running water might prove dangerous at sulfate concentrations of less than 150 mg/ℓ. Increased hydrostatic pressure might decrease permissible sulfate concentrations still further.

- Solutions of calcium sulfate may react directly with the tricalcium aluminate (C_3A) component of hardened cement to form highly hydrated calcium sulfoaluminates ($C_3A \cdot 3CaSO_4 \cdot 31\text{-}32\ H_2O$). The product has a much higher specific volume than the reactants, which can lead to swelling of the concrete to its eventual fracture. Other soluble sulfates (e.g., Na_2SO_4) can react to form the voluminous calcium sulfoaluminates.

The conversion of calcium hydroxide to gypsum and the combination of gypsum with hydrated C_3A to form calcium sulfoaluminate produces a molecular volume of product nearly double that of the reactants. However, the formation of products with higher volume than the reactants does not necessarily cause a structure to expand and fracture. There are other mechanisms through which volume increases may be accommodated (35).

- Magnesium and ammonium sulfates are particularly corrosive to concrete because of the following reactions with $Ca(OH_2)$, in one case by precipitation of insoluble $Mg(OH)_2$ and in the other by volatilization of ammonia:

  $$MgSO_4 + Ca(OH)_2 \rightarrow CaSO_4 + Mg(OH)_2\downarrow$$

  $$(NH_4)_2SO_4 + Ca(OH)_2 \rightarrow CaSO_4 + 2H_2O + 2NH_3\uparrow$$

  As a result, further amounts of $Ca(OH)_2$ will be liberated by breakdown of calcium hydrosilicates.

Based on the above principles, two approaches have been used to increase the sulfate resistance of concrete. One is steam curing under pressure at temperatures above 100°C, which reduces the free $Ca(OH)_2$ by promoting its reaction with siliceous aggregates to form hydrated mono-calcium silicate (35). Resistance to sodium sulfate corrosion is thus increased dramatically. Resistance to magnesium sulfate corrosion is less striking because $MgSO_4$ can still attack hydrated calcium silicates as discussed above. Steam curing is not universally applicable because it cannot be applied in situ, but only to precast concrete units.

The second approach has been to decrease the C_3A content of the cement below 5%. ASTM Type V cement meets this requirement, but the degree of sulfate resistance imparted is still a subject of some controversy. Among the portland cements the Ferrari grade in which essentially all of the C_3A is reacted with ferric oxide to form tetracalcium aluminate ferrite (C_4AF) has been reported to provide optimal sulfate resistance, with no sign of corrosion in a sewer line during 25 years of exposure to 15,500 ppm SO_4.

Work by the U.S. Army Corps of Engineers has shown that addition of fly ash pozzolan to Type I portland cement yields a product, termed Type 1-P, which shows increased sulfate resistance approximatley equivalent to a Type II cement (21). The Corps has conducted a number of use test on such cements in relatively low sulfate waters which indicated good potential for use of these materials.

There has been very little experience with the use of unlined concrete tanks in FGC systems that would provide some indication of the corrosion potential of FGC liquors and leachates. A number of systems do utilize vessels constructed partially or wholly of concrete or cement as scrubber liquor recycle tanks and thickeners. Most of these are lined with protective coatings such as polyester flake lining or epoxy resins. A few, though, without linings are in operation. A direct lime scrubber system at Louisville Gas and Electric Company's Cane Run Station has scrubber recycle tanks and a thickener floor constructed of unlined Type II cement. These have been in service since the mid-1970's with little evidence of corrosion. However, the system operates in a semi-open loop in that waste solids are discharged from the system as a thickened slurry containing up to 25-30 wt % solids, so there the buildup in concentrations of dissolved solids in the liquor rarely exceeds the range of 1500-2500 ppm (mostly calcium chloride and sulfate).

In order to gain some perspective on corrosion potential, results of corrosion testing performed in somewhat analogous environments are reviewed below.

- Sulfate Corrosion (Seawater)--Although seawater is comparable to waste liquors in sulfate and calcium levels, it typically has much higher levels of chloride (except for FGD systems on high chloride content coals), magnesium (FGD wastes only contain appreciable magnesium when it has been deliberately added to improve lime/limestone scrubber operation), potassium and sodium (except for sodium-based scrubber systems). The deterioration of concrete in seawater has been ascribed primarily to the action of magnesium sulfate (35). The results of sulfate deterioration of concrete in seawater are sufficiently different from other types of sulfate corrosion so that there is little basis for predicting deterioration of concrete based on seawater results except for waste liquors containing very high levels of magnesium and TDS levels of 30,000-40,000 ppm.

- Sulfate Corrosion (Groundwater)--Many naturally occurring soils are high in sulfate, sometimes containing several percent of sodium, potassium, magnesium, and calcium sulfates. Groundwaters in such soils can contain as much as 1% SO_4 (10,000 ppm). There has been a great deal of work done on corrosion of concrete in sulfate soils, but the results have been less than definitive. The two factors which seem to be of major importance to concrete stability in sulfate soils are: the cement content of the concrete and the C_3A content of the portland cement. The rate of deterioration for a given C_3A content decreases as the cement content increases. For a given cement content, performance improves as the C_3A content is decreased. The relative degrees of attack on concrete by soils are listed in Table III-8. Sulfate concentrations in FGC waste liquors would often correspond to conditions of severe attack.

TABLE III-8

ATTACK ON CONCRETE BY SOILS AND WATERS CONTAINING VARIOUS SULFATE CONCENTRATIONS

Relative Degree Sulfate Attack	Water-Soluble Sulfate (as SO_4) in Soil Samples	PPM of Sulfate (as SO_4) in Water Samples
Negligible	0.00 to 0.10	0 to 150
Positive[1]	0.10 to 0.20	150 to 1,000
Considerable[2]	0.20 to 0.50	1,000 to 2,000
Severe[2]	Over 0.50	Over 2,000

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[1] Use Type II cement.

[2] Use Type V cement.

(Source: 38)

- Sulfite Corrosion--There is much less information in sulfite corrosion than about sulfate corrosion. In tests of mortars under conditions of continuous immersion in static solutions at room temperature, 0.1 N sodium sulfite ($\sim$12.6 g/ℓ) proved to be at least as aggressive as 0.1 N sodium sulfate ($\sim$14.2 g/ℓ). Type V cement mortars resisted attack by 90%-saturated Na_2SO_3 solutions for 15 months.

- Chloride Corrosion--After 15 months of immersion in 90%-saturated NaCl solutions, test mortars with Type V cement showed virtually no evidence of corrosion.

- Bisulfate and Bisulfite Corrosion--Acids will generally attack concrete by dissolving constituents of portland cements and forming soluble salts. However, dissolution of lime into dilute static acid solutions usually results in a fairly rapid increase in pH. Nonetheless, initial acid dissolution can increase the porosity of concrete and open it up to more rapid sulfate attack. Static solutions of $NaHSO_4$, 90% saturated, maintained a pH of less than 1 in contact with cement mortars and resulted in rapid failures even for Type V cements. Even in 0.1N $NaHSO_4$, no mortars lasted longer than seven months. Sodium bisulfite proved to be more corrosive to some mortars than $NaHSO_4$ but not to others.

- Corrosion of Steel Reinforcements

  Concrete, in principle, can provide reasonably good protection of embedded steel reinforcement against corrosion. The concrete provides an alkaline atmosphere that favors formation and maintenance of a thin passivating oxide film on the surface of the steel. When failures have occurred, they have generally been attributed to one or more of the following:

  - cracks in the concrete which permit rapid penetration of moisture, air, and/or chemical solutions;

  - electrolysis caused by electrical leakage or improper grounding in the presence of an electrolyte in contact with concrete;

  - corrosion cells set up as a result of potential differences in various parts of a reinforced concrete.

  Slow permeation of chemical corrosive to steel can also occur. Chlorides, for example, can be very detrimental to the protective oxide film that forms on reinforcing steel. Type V cement is less protective against chloride corrosion of steel than Type I, although Type V is recommended for sulfate resistance. Type I is more protective because of its higher C_3A content. C_3A retards chloride migration by its reaction with chloride forming calcium chloroaluminate. Type 1-P, with its increased sulfate resistance and only slightly lower C_3A content should also provide protection against chloride corrosion.

> Concretes of low permeability can provide the best protection to steel reinforcing rods as well as a degree of protection against corrosion of the concrete itself. Low water/cement ratios (less than 4.5 gals./sack) are favorable to low permeability, and adequate moist curing prior to use is essential.

Drawing upon the above information on concrete corrosion in analogous environments, it is apparent that FGC waste liquors and leachates do have potential for corrosion of concrete and possibly reinforcement steel embedded in the concrete. The severity of attack (rate and extent) will be highly dependent upon the composition of the waste, the characteristics of the mine water contacting the waste, and the type of concrete used. The presence and concentration levels of chloride, sulfate, magnesium, and overall acidity (pH) are prime concerns, although other species can participate in or inhibit corrosion reactions. Corrosion specialists at the Portland Cement Association have indicated that it is difficult to predict the degree and mechanism of corrosion of concrete by FGC wastes without laboratory testing covering the range of concentration levels of various species. Differences in the species present and their relative concentrations can result in antagonistic or synergistic effects on corrosion.

Lacking such data, there are still some broad conclusions which can be drawn regarding corrosion potential of FGC wastes and corrosion prevention based upon information available:

- Wastes with liquors containing only a few thousand ppm or less of dissolved solids will probably not present any significant corrosion problems, especially if magnesium levels are relatively low.

- Acidic FGC wastes will probably require, as a minimum, neutralization with lime or limestone. If they are to be disposed in an acidic mine water environment, then either additional lime or limestone needs to be added (prior to disposal or to the waste), or the waste may require stabilization.

- Precast steam-cured concrete sections may be used for bulkhead construction in critical areas, if possible, where wastes contain high levels of sulfate (as sodium, potassium, or calcium salts).

- Stabilized or otherwise treated wastes may be preferentially placed in the immediate vicinity of bulkheads, with disposal of untreated wastes in other areas.

Certainly, for wastes containing high levels of dissolved solids (or of particular species) or where wastes are to be placed in acidic underground mine environments with high groundwater flows, testing of corrosion potential will be necessary if concrete bulkheads are to be used. In such testing, consideration needs to be given not only to the liquors contained in the wastes but also leachates resulting from expected water infiltration characteristics of the mine environment.

C. CONCLUSIONS AND RECOMMENDATIONS

1. Physical and Chemical Impact Considerations

The overall conclusions of the initial assessment are still considered valid (1). The disposal of FDG wastes in mines is feasible from a technical standpoint, and there are practical options available in terms of waste processing, placement and site management to control potential adverse environmental impacts in most cases. However, the viability and environmental impacts of each disposal situation must be evaluated based upon its specific hydrogeology of the site, waste characteristics and placement method.

Specific conclusions regarding the issues and impacts addressed in this refined assessment are discussed below.

a. Stability

The requirements for physical stability of waste deposits in surface mine disposal operations depend upon the type of disposal operation, the mine characteristics, and the method of mining employed. In general, it would be expected that most wastes at solids levels near optimum moisture content would have physical and engineering properties adequate to ensure acceptable stability (e.g., resistance to flow under its own weight, due to disturbances from mining activities, etc.). In the case of sulfite-rich wastes, this could easily necessitate admixture of filtered (or centrifuged) waste with some amount of fly ash. Where the FGD waste solids cannot be adequately dewatered and there is insufficient fly ash available for stabilization, admixture of both fly ash and lime may be required. However, simply the addition of lime may not ensure short-term stability (prior to curing) if the waste is too wet. In such cases, stockpiling of the waste may be required to allow time for curing to begin (which also increases solids content) prior to disposal. Other control measures available, depending upon the type of disposal, to minimize stability problems include: production of gypsum rather than sulfite-rich material; mixing of wastes with soil/overburden; control of placement to minimize rewetting (and saturation); and creation of containment walls of overburden either during disposal or after disposal (e.g., by placing the waste in discrete areas or on one side of the pit).

b. Freeze/Thaw Affects

Freezing of wastes may alter the chemical as well as physical properties of wastes, which can affect handlability and ultimate strength developed. Laboratory testing of untreated waste samples indicated no significant affect of freeze/thaw on drainage of water from the waste. The degree of freezing and the affects of freezing on handlability can be minimized by dewatering (and admixture with ash) to achieve near optimum moisture content. For areas of the country exhibiting extreme temperature conditions, use of heated trucks may be required (e.g., piping exhaust through truck walls) to ensure handeability.

Freezing would normally be expected to slow curing rates of stabilized wastes. If it occurs prior to the onset of curing, freezing may severely reduce the ultimate strength achieved. If it occurs after initiation of curing, there may be little or no effect on hardening. In order to increase curing rates and ultimate strength under winter conditions, it may be desirable to stockpile the waste for additional time (four to seven days) to allow onset of curing before disposal.

c. Fugitive Emissions

Although possibly, emissions of dust from FGC wastes in mine disposal operations are unlikely due to relatively high moisture content. Fugitive dust emissions from stockpiles can be relatively easily controlled. Drying of waste pile surfaces will usually result in crustation; however, should dust emissions result, they can be minimized by wetting the surface in much the same way dirt road surfaces are wetted.

d. TOS Dissolution

Dissolution of calcium sulfite from sulfite-rich FGD wastes can result in TOS levels in leachates ranging from tens to hundreds of ppm depending upon groundwater ionic strength, acidity and hardness. This can result in levels of COD sufficient to deplete dissolved oxygen in groundwater and affect local receiving waters. Where sulfite-rich waste deposits can impact aerobic ground and surface waters, the solubility of TOS must be a consideration in the impact of waste leachate. In many cases, the concentration of TOS, which represents an immediate oxygen demand, may not result in significant reductions in dissolved oxygen due to low leachate rates.

e. Offgassing Potential

There is potential for offgassing CO_2, SO_2, H_2S and possibly other gases from waste deposits in mines, particularly in underground mines. The release of SO_2 and H_2S are of greatest concern.

SO_2 offgassing can result from contact of neutral or slightly basic, sulfite-rich wastes with highly acidic mine waters (pH $<\sim 3.0$), especially during initial disposal operations where the quantity of waste is relatively small compared to the amount of water. Longer-term evolution of SO_2 is less likely to occur, but also more difficult to predict as a generalization. The potential for short-term evolution can be minimized by (1) avoiding placement of sulfite-rich wastes in mine areas containing highly acidic drainage, (2) pumping out and treatment of water prior to placement, (3) pre-neutralizing water with limestone or (4) increasing the alkalinity of the waste by admixture of lime or limestone. Minimizing infiltration and/or acidification of groundwater in the mine by (1) maximum filling of voids, (2) use of bulkheads or (3) reduction of waste permeability by use of stabilization will also help prevent long-term SO_2 offgassing potential. If the waste is stabilized by admixture of fly ash and lime prior to disposal, additional lime may be required to also negate the effects of the acid water on curing of the waste.

Release of H_2S from FGD wastes has been noted in a number of instances. Laboratory testing has also indicated the potential for H_2S release. It can occur from either sulfate- or sulfite-rich materials due to the activity of facultative anaerobes such as sulfate-reducing bacteria. Some of the same measures used to control SO_2 offgassing may also be appropriate for H_2S offgassing. These include: proper selection of disposal sites and disposal sites and disposal methods; waste stabilization prior to disposal; and, in the case of underground disposal, maximum filling of voids and use of bulkheads to reduce contact with water.

f. Bulkhead Corrosion

Use of bulkheads as containment walls may be required in some areas of underground mine disposal operations. If constructed of concrete, these may be susceptible to chemical attack by FGC liquors. Deterioration would be expected to be most severe for acidic wastes, especially those containing high levels of dissolved solids (e.g., sodium, magnesium, chloride and sulfate). At present there is very little information on cement and concrete behavior in the presence of liquors similar to those that might result from closed-loop operation of FGC systems. Parametric corrosion testing needs to be performed to assess the effects of FGC wastes and to develop a data base sufficient for specifying adequate cement/concrete mixes. Such testing needs to cover realistic and extreme ranges of scrubber liquors and leachate composition. Of particular importance would be concentrations of chloride, sulfate, fluoride, sulfite, sodium and magnesium, and pH.

Measures which can minimize the potential for deterioration of concrete bulkheads include: coating of imbedded steel in reinforced structure; reduction in leachate generation by maximum filling of voids and/or waste stabilization; and increasing the alkalinity of the waste to avoid developing acidic conditions.

2. Need for Additional Research and Information

Research needs include (1) field-scale demonstration of promising surface mine and underground mine disposal and (2) monitoring of full-scale, ongoing operations to establish practical disposal methods and evaluate actual environmental impact potential (both detrimental and beneficial). One such demonstration and monitoring program is currently underway at the Baukol-Noonan mine in Center, ND. This surface mine disposal demonstration program has been funded by the U.S. EPA, and results will be published in separate reports.

Additional testing of waste properties and impact potential under controlled conditions is also desirable to enable a better prediction of disposal requirements and waste behavior. Important among these are the following:

- Additional triaxial compression and dynamic load testing on a variety of different wastes (including dry sorbent wastes) and for a range of moisture levels. This will provide a better indication of the degree of dewatering and/or fly ash addition required for disposal of untreated wastes and the effects of variability on handling and stability of the wastes.

- Performance of leaching column tests using mine waters and overburden materials to assess potential pollutant mobility in mining environments, as well as potential for improvement of mine drainage. This is best performed in concert with demonstration testing or as a part of a full-scale monitoring program. A limited amount of such testing has been performed by Michael Baker Jr., Inc., Twin City Testing, and the University of North Dakota (as part of the Center, ND demonstration program).

- Performance of testing to evaluate the effects of FGC waste liquors and leachates on cement and concrete.

CHAPTER III REFERENCES

1. Lunt, R.R., et al. "An Evaluation of the Disposal of Flue Gas Desulfurization Wastes in Mines and the Ocean: Initial Assessment," A report to the U.S. Environmental Protection Agency, EPA-600/7-77-051, May 1977.

2. Johnston, P.H., "The Effect of Fly Ash Addition on the Geotechnical Properties of Flue Gas Desulfurization Sludges," M.E. Thesis, University of Louisville, Louisville, Ky, 1978.

3. Coones, C.M., "Pumpability of Flue Gas Desulfurization Sludges," M.E. Thesis, University of Louisville, Louisville, Ky, 1978.

4. Bodner, B.S., "The Effects of Lime and Fly Ash Addition on the Geotechnical Properties of FGD Sludges," M.E. Thesis, University of Louisville, Louisville, Ky, 1978.

5. Hagerty, D.J., et al, "Engineering Properties of FGD Sludges," Proceedings, Special Conference on Geotechnical Practices for Disposal of Solid Waste Materials, ASCE, Ann Arbor, Michigan, June, 1977.

6. Schumann, M., "An Evaluation of the Stability of SO_x Sludge Deposits Including Their Response to Ground Motion," M.E. Thesis University of Louisville, Louisville, Kentucky, 1977.

7. Thacker, B.K., "Geotechnical Properties of Flue Gas Desulfurization Sludges," M.E. Thesis, University of Louisville, Louisville, Kentucky, 1977.

8. Jones, B.F., et al, "Evaluation of the Physical Stability and Leachability of Flue Gas Cleaning Wastes," A study for EPRI, Research Project No. 786-2, Palo Alto, California, January, 1979.

9. Rosoff, J., et al, "Disposal of By-Products from Nonregenerable Flue Gas Desulfurization Systems: Second Annual Progress Report," A study for the U.S. Environmental Protection Agency, EPA-600/7-77-052, May, 1977.

10. Leo, P.P., and J. Rosoff, "Control of Waste and Water Pollution from Coal-Fired Power Plants: Second R&D Report," A study for the U.S. Environmental Protection Agency, EPA-600/7-78-224, November, 1978.

11. Haas, J.C. & Ladd, "Environmentally Acceptable Landfill from Air Quality Control System Sludge," Frontiers of Power Technology Conference, Oklahoma State University, Stillwater, Oklahoma, December, 1974.

12. Klym, T.W. and D.J. Dodd, "Landfill Disposal of Scrubber Sludge," National ASCE Environmental Engineering Meeting, Kansas City, Kansas, October, 1974.

13. Krizek, R.J., et al, "Characterization and Handling of Sulfur Dioxide Scrubber Sludge with Fly Ash," Eng. Foundation Conference, Hueston Woods, Ohio, October, 1976.

14. Krizek, R.J., et al, "Engineering Properties of Sulfur Dioxide Scrubber Sludge with Fly Ash," Eng. Foundation Conference, Hueston Woods, Ohio, October, 1976.

15. Mahloch, J.L., et al, "Pollutant Potential of Raw and Chemically Fixed Hazardous Industrial Wastes and Flue Gas Desulfurization Sludges," Interim Report to the U.S. Environmental Protection Agency, EPA-600/2-76-182, July, 1976.

16. "Laboratory Testing of Sludge, Fly Ash, Lime and Bottom Ash Mixtures," Twin City Testing and Engineering Laboratory, Inc., St. Paul, February, 1976.

17. Rush, R.E. and R.A. Edwards, "Evaluation of Three 20-Mw Prototype Flue Gas Desulfurization Processer," A report to EPRI, EPRI FP-713, Project 536-1, Final Report, March, 1978.

18. Edwards, R.A. and R.C. Reed, "CEA Dual Alkali FGD Sludge/Fly Ash and Sludge/Fly Ash/Lime Landfill and Compaction Demonstration," The Southern Company Services, Inc., Birmingham, Alabama, April, 1977.

19. LaMantia, C.R., et al, "Final Report: Dual Alkali Test and Evaluation Program," Vol, III, EPA-600/7-77-050c, May, 1977.

20. Elnagger, H.A., and J.G. Selmeczi, "Properties and Stabilization of SO_2 Scrubbing Sludges," Proc., 1st Symposium Coal Utilization, NCA/BCR, Louisville, Kentucky, October, 1974.

21. Santhanam, C.J., et al, "Waste and Water Management for Conventional Coal Combustion - Assessment Report," EPA-600/7-80-012c, 1980.

22. Mitchell, J.K., Fundamentals of Soil Behavior, John Wiley and Sons, Inc., 1976.

23. "Scrubbing Testing and Waste Disposal Studies," Progress Report prepared by Louisville Gas and Electric Company, EPA Contract No. 68-02-2143, 1977-78.

24. Personal Communication, Dravo Corporation, 1978.

25. Personel Communication, H. Mullen, IUCS, 1978.

26. Cowherd, C., "Development of Emission Factors for Fugitive Dust Sources," MRI, EPA-450/3-74-037, June, 1974.

27. Drinker, P., and T. Hatch, Industrial Dust, Hygienic Significance, Measurement, and Control, McGraw Hill, New York, 1954.

28. Personal Communication, Dr. R. G. Vranka, Arthur D. Little, Inc., Cambridge, Massachusetts, October, 1977.

29. Holland, W.F., et al, "The Environmental Effects of Trace Elements in the Pond Disposal of Ash and Flue Gas Desulfurization Sludge," EPRI Project 202, Palo Alto, California, September, 1975.

30. Bartos, Jr., M.J., and Palermo, M.R., "The Physical and Engineering Properties and Durability of Raw and Chemically Fixed Hazardous Industrial Wastes and Flue Gas Desulfurization Sludges," U.S. Army Engineer Waterways Experiment Station, Vicksburg, Mississippi, Interagency Agreement No. EPA-IAG-D4-0569, 1977.

31. Rosoff, J., et al, "Disposal of By-Products from Nonregenerable Flue Gas Desulfurization Systems: Final Report," EPA Contract No. 68-02-4010, U.S. Environmental Protection Agency, March, 1978.

32. "Characterization Study of LG&E's Paddy's Run Flue Gas Desulfurization System," Draft Final Report, Radian Corp., EPA Contract No. 68-02-2102, 1978.

33. Colpharp, W.M., et al, "Chemical/Physical Stability of Flue Gas Cleaning Wastes," Radian, EPRI FP-671, 1979.

34. "Durability of Concrete in Service," ACI Committee 201 Report, ACI Journal, Proceedings V.59, No. 12, December, 1962.

35. Lea, F. M., Chemistry of Cement and Concrete, Chemical Publishing Co., Inc., 1971, N.Y., N.Y.

IV. DISPOSAL AT SEA

A. BACKGROUND

1. Impacts and Issues Identified in the Initial Assessment

In the initial assessment of the disposal of FGC wastes in the ocean (1), four principal categories of potential environmental impacts and three aspects of the existing regulatory framework were identified as significant issues. The four environmental impact categories of concern were:

- effects of disposed wastes on the quality of benthic habitat;
- biological, physical and chemical impacts of descending or suspended wastes in the water column;
- sulfite-related toxicity and oxygen depletion in the vicinity of masses of certain FGC wastes; and
- contamination of the water column and/or benthic habitat by trace elements from the wastes.

The three aspects of the regulatory framework judged to be of special significance were:

- definitions of limiting permissible concentrations in disposal area "mixing zones";
- absolute limits on permissible concentrations of mercury and cadmium in solid fractions of waste materials; and
- potential disincentives to deep ocean (i.e., off-shelf) dumping.

2. Findings and Conclusions of the Initial Assessment

The initial assessment resulted in a series of technical/environmental and regulatory conclusions and recommendations, as discussed below.

a. Technical/Environmental Considerations

With regard to the technical feasibility and environmental impacts of FGC sludge disposal, two overall and three more specific conclusions emerged. These were as follows:

(1) Overall

- There is an overriding need for a case-by-case approach to the analysis of the environmental feasibility of ocean disposal of specific FGC wastes. The emphasis in such analyses should be twofold, focusing both on the type of waste and the disposal site environmental conditions.

- All four control options considered appeared to be technically feasible. These were:
  - dispersed dumping on the continental shelf;
  - conventional dumping in the deep ocean (off the continental shelf);
  - dispersed dumping off the continental shelf; and
  - concentrated dumping of treated sludges on the continental shelf.

The economic feasibility of these control options was regarded as less clear-cut and would serve to limit the viability of several of the more promising options.

(2) Specific

- Unless further work contradicts anticipated sedimentation and suspension impacts, the disposal of untreated or treated FGC wastes with soil-like physical properties by bottom-dump barge or outfall on the continental shelf should be considered environmentally undesirable.
- Based upon available information on sulfite toxicity, it appears that an almost immediate (on the order of minutes) dilution factor greater than 10,000:1 for sulfite alone is required in the dispersed disposal of untreated wastes containing large fractions of sulfite. The technology is not available for attaining such dilution factors for untreated sulfite-rich wastes in an economical manner. Therefore, the dispersed disposal of sulfite-rich wastes both on and off the continental shelf was not considered to be a promising option at the time. Further information on organism uptake and toxicity of TOS could justify reevaluation of this conclusion.
- Several disposal options appeared promising and were recommended for further research. These included:
  - dispersed disposal of untreated sulfate-rich FGC wastes on the continental shelf;
  - concentrated disposal of treated brick-like FGC waste on the continental shelf;
  - dispersed disposal of untreated sulfate-rich FGC wastes in the deep ocean; and
  - concentrated disposal of both untreated sulfate-rich FGC wastes and treated FGD wastes in the deep ocean.

b. Recommendations for Additional Research

The research needs considered most important at the conclusion of the initial assessment were the following:

- A body of empirical data needed to be developed concerning the physical fate and dissolution rates of various types of treated and untreated FGC wastes in representative conditions that would characterize the disposal area environs.
- Empirical values for exposure of both liquid and solid constituents of FGC wastes to various marine organisms needed to be developed. In particular, values associated with short-term exposure of pelagic organisms required investigation.
- Lethal and sublethal effects thresholds needed to be developed for a variety of representative marine organisms upon exposure to FGC wastes. One of the focal points of such research should be the dynamics of food web transfer of potential toxicants contained in some FGC wastes as trace contaminants.
- Mechanisms for eliminating existing economic disincentives to deep ocean disposal should be developed. These could include consideration of such options as a greater federal role in baseline and disposal area monitoring.

3. Purpose, Scope, and Approach of This Refined Assessment

Given the impacts, issues, and conclusions of the initial assessment, the objectives of this refined assessment were:

- performance of limited laboratory testing designed to supply additional information required for an accurate description of the fate of FGC wastes in the various ocean disposal options under study and contribute to the design of subsequent simulation/demonstration testing; and
- refinement and adjustment of the initial impact assessment to the extent that new information and data allow.

While consideration of all aspects of the initial assessment are generally within the scope of this effort, attention was focused on the physical and chemical issues and impacts identified in the initial assessment. Less emphasis was placed on the preparation of cost estimates and the broader spectrum of biological impacts than in the initial assessment. Subsequent testing will address biological impacts in much greater detail.

Laboratory testing and related assessment efforts involved three areas of investigation:

- physical fate of FGC wastes in the water column;
- physical fate of FGC wastes on the ocean bottom; and
- chemical fate of untreated FGC wastes in seawater.

For the most part, this work concentrated on the fate and effects of untreated sludges because of the lack of definitive data on their behavior in ocean environments. Table IV-1 lists the suite of FGC waste samples used in the laboratory testing.

In-house tank tests were designed to investigate physical fate in the water column. These tests focused on the manner in which FGC wastes of different physical and chemical properties behaved while descending through a seawater column and immediately upon impacting a surface representing the ocean floor. Measurements were conducted to determine residual concentrations of suspended solids in the water column at varying time intervals during and after each drop. Efforts were then made to scale the results of these experiments for use in predicting the fate of dumped FGC wastes in actual ocean environments.

A test program designed by Arthur D. Little, Inc. and the research staff of the New England Aquarium was conducted using the facilities of the Aquarium to investigate the physical fate of FGC waste on the ocean bottom. Information gained from the water column tests and the continuing update of the impact assessment was used to select appropriate materials for the Aquarium test program. Dredged material which had been subjected to previous testing of this nature was used to provide a reference point for interpretation of the results of tests using waste materials, and FGC wastes representing opposite ends of the spectrum of cohesivity were chosen. Specific parameters investigated in these latter tests included critical velocities for erosion of the test materials and residual concentrations of the materials both on the bottom and suspended in the test water column.

TABLE IV-1

MAJOR CHEMICAL CONSTITUENTS OF FGC SLUDGE SAMPLES USED IN LABORATORY TESTING (%)

Sludge	Date Shipped	Description	Wt. % Solids[1]	Ca	TOS[2]	SO_4	Na	Mg	Cl	Acid Insol.[3]	OH
DA1	6/26/76	Dual Alkali, filter cake (no ash)	54	7.15	5.52	0.97	0.43	0.25	0.037	0.00	0.5
DA2	6/24/76	Dual Alkali, filter cake (no ash)	62.7		5.88						1.0
DA3	7/2/76	Dual Alkali, filter cake (flyash)	57	4.45	2.66	0.87	0.22	0.22	0.031	30.8	
LS1	6/17/75	Limestone, filter solid	56.6	6.48	3.04	0.64	0.03	0.07	0.09	24.9	
L1	9/10/76	Lime, centrifuge cake (flyash)	63	4.59	3.85	0.70	0.03	0.045	0.052	35.2	
L2	9/10/76	Lime, Vent. filter cake (no ash)	52	7.22	5.76	1.37	0.03	0.074	0.030	0.83	
LS3	2/03/77	Limestone, Vent. filter cake (flyash)	79.3	4.20	0.01	3.69	0.03	0.04	0.05	37.6	
LS2	1/20/77	Limestone, clarifier-underflow (no ash)	58.7	7.06	5.24	0.99	0.03	0.07	0.09	6.4	
DA4	7/75	Dual Alkali (inadvertently air dried)	97.6	7.32	5.28	1.14	0.19	0.15	0.02	2.5	
DA5	7/75	Dual Alkali (inadvertently air dried)	98.5	7.56	4.96	1.42	0.23	0.13	0.03	4.4	
L3		Direct Lime, filter cake (carbide)	47	6.99	5.89	0.52	0.02	0.23	0.008	2.9	
G1		Gypsum	83	6.05	----	6.04	0.02	0.012	0.004	0.30	
DA2	(washed)	Dual Alkali (washed with distilled water)			5.90						0.8

[1] Weight percent dry solids in the as received wet cakes
[2] Total Oxidizable Sulfur (calculated as sulfite)
[3] Insoluble in 1 molar HCl

Source: Arthur D. Little, Inc.

Several of the major unanswered questions raised by the inital assessment concerned the dissolution and oxidation rates of sulfite-rich wastes and to a lesser extent the dissolution rates of other types of FGC wastes. Chemical testing was performed at Arthur D. Little, Inc. to determine the dissolution and oxidation rates of selected sulfite-rich FGC wastes in seawater. In addition to being incorporated into the continuing impact assessment, these results along with those of the water column and bottom tests will provide the basis for the design of forthcoming chemical and biological testing to be conducted as part of the simulation/demonstration program.

The approach to further evaluation of those impact issues investigated outside the laboratory consisted of a combination of updated literature review and a series of technical/regulatory interviews with key individuals involved in ocean dumping research and regulatory programs around the country. Field visits included follow-up contacts with certain key personnel in the EPA offices of Marine Protection and General Counsel in Washington and EPA's Environmental Research Laboratories. Ocean dumping regulators were interviewed in Regional EPA offices in New York (II), San Francisco (IX), and Dallas (VI). Researchers involved in sediment transport studies in San Francisco Bay and at NOAA's Miami facilities as well as investigators involved in studies of trace contaminant mobilization and uptake at the Southern California Coastal Waters Research Project (SCCWRP) in Los Angeles were also interviewed.

Additional field and laboratory investigations were conducted at the location of an inadvertent FGC waste discharge into a shallow marine embayment in Southern Florida. Information obtained from this element of the work program has answered several major questions concerning the potential long-term fate of ocean-dumped FGD materials. This information has obviated several additional studies in the laboratory. The subsequent work performed in this assessment has answered some of the questions raised by the initial assessment in each of the categories. However, definitive evaluation of the impacts in each category still requires the type of information available only through field observations and, to a less extent, bioassay testing. The results reported at this time have provided an excellent basis for forthcoming bioassay experiments, which are expected to provide virtually definitive results concerning

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the impact potentials of the more promising disposal options. The questions which will remain unanswered at the laboratory scale are expected to revolve around the extent to which adverse effects observed at that scale would be repeated in the actual ocean environment. The discussion below summarizes the findings of this phase of the continuing assessment and previews the manner in which the subsequent testing is expected to provide information suitable for the review of specific disposal actions.

B. REFINEMENT OF THE ENVIRONMENTAL ASSESSMENT

1. Physical Fate and Effects

a. Introduction

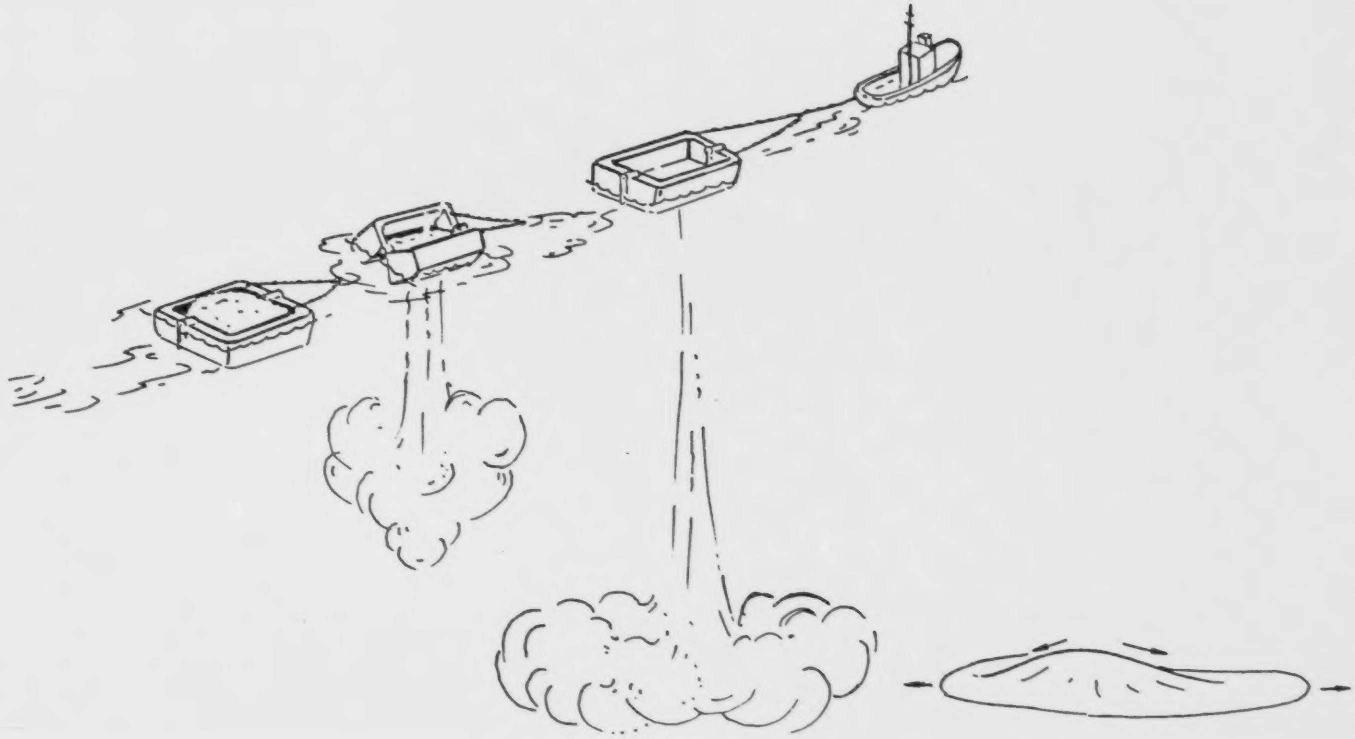
The physical fate of FGC wastes in ocean environments was identified in the initial assessment (1) as an area requiring further research. The disposition of FGC wastes after release to the sea from bottom-dump vessels was of particular concern. Further study was needed to determine more accurately the behavior of FGC waste in the water column and to identify the processes important to short- and long-term transport and distribution throughout the various ocean environments. This was because the severity of impacts in each of the four environmental impact categories of concern (See Background discussion above) would in large part be determined by the physical fate of the waste in the ocean. Specifically, amounts and concentrations of waste expected to be present at predictable locations for predictable amounts of time needed definition.

In general, all unconfined materials dumped into the ocean undergo the following generalized transport phases (see Figure IV-1):

- Convective descent--characterized by the material falling through the water under the influence of gravity and its own momentum. Entrainment of ambient water into the body of falling material occurs during this phase;

- Collapse--the cloud spreads into a relatively thin layer when either the bottom or water that is encountered is more dense than the cloud; and

- Long-term transport--the spreading or settled material undergoes long-term diffusion in the water column and/or erosion of bottom deposits.



Barge -	Loaded, underway	Dumping, barge in hinge-open position	Empty, underway	
Waste -		Convective	Collapse phase	Long-term spreading phase

FIGURE IV-1 SCHEMATIC DIAGRAM SHOWING DUMPING OPERATION-HINGED BOTTOM-DUMP BARGE

Source: Arthur D. Little, Inc.

Of these generalized categories the convective descent and collapse are short-term phases completed within several minutes to several hours after a material drop. The long-term transport phase, on the other hand, may continue for many years. A relatively complete understanding of these phases would allow the determination of a "waste budget," i.e., a detailed account of the waste distribution during and after the drop. Such a waste budget could specifiy the amount of sludge reaching the bottom during the short-term phases, the amount left suspended in the water column, and the amount dissolved. The waste budget would be expected to vary with the characteristics of the material and disposal site conditions. In this refined assessment the initial drop through the water and the mobility of FGC waste on the bottom were addressed in laboratory simulation testing and theoretical analyses. Additional insight into the long-term behavior of waste in the ambient environment was derived from further field observations of an inadvertent discharge of FGC waste into a shallow marine embayment.

b. Investigations of FGC Waste Behavior During Descent and Collapse

(1) Description of Short-Term Phases (Convective Descent and Collapse)

It has been observed that a single fine-grained particle whose density is greater than that of water will fall slowly through a body of water with a characteristic fall velocity. In general, the smaller the particle, the slower the fall velocity due to the dominance of friction. However, when a mass of fine-grained particles is packed together and then collectively dumped into a body of water, it is apparent that the fall behavior of each particle will be strongly influenced by the surrounding particles and that the observed behavior will bear little resemblance to the slow fall of a single fine-grained particle. In dropping a collection of particles as opposed to a single particle, two new physical effects are observed, namely, a cohesion effect and a density effect.

Cohesion causes the individual particles in the descending mass to actually stick together. Thus, as a result of cohesion, a lump of clay will fall as one lump instead of as individual clay particles. A true cohesion effect is generally exhibited among particles with high specific surface areas (surface area per unit weight) by virtue of the physicochemical surface forces which exist among them. The dominance of physicochemical cohesiveness is a function of particle size, shape, and chemistry. In general, the smaller the particle size, the greater the influence of true cohesion. However, particle morphology (including shape) is equally important. For example, a quartz sphere of 1 mm diameter has a specific surface area of nearly 0.0023 m^2/gm, whereas the specific surface area of a sodium-substituted montmorillonite (approximately the same size) is about 750 m^2/gm (2).

A similar effect, known as apparent cohesion, can also be observed in materials whose handling leads to the development of capillary tensions in the pore waters. Apparent cohesion is discussed in greater detail later under Modeling.

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The density current effect results from the complex interaction between the ambient water and the dense collection of falling particles. When one small particle falls through a body of water, the mass of water about it is relatively stationary. However, when many particles are introduced into the water in a dense mass, the sum of the friction forces exerted by the particles on the water causes an entrainment of water. Consequently, the water among the falling particles is not stationary but is moving downward with the particles.

In relation to the surrounding water this mass of falling particles and entrained water acts as a liquid of greater density and falls as a density current. Since ambient water is continually entrained into this mass or cloud, the difference in density between the cloud and the surrounding water decreases continually as the cloud falls.

If the ambient water is stratified, the waste cloud could reach a neutrally buoyant position about which it would oscillate as it entered the collapse phase. If not, then the waste cloud would continue downward until it hit bottom.

The cohesion effects and the density current effect cause the particles in a mass to fall through water as a unit rather than individually. As a consequence, material experiencing these effects will fall a great deal faster than material introduced into the water column as discrete particles.

(2) Laboratory Observations

In general, the above effects (density current and cohesion) and the fall of individual particles were observed in the laboratory-scale experiments simulating bottom-dump barge drops of FGC waste. These experiments are described in detail in Appendix B.

The simulated drop tests were conducted in a 20-gallon aquarium (36" high x 12" x 12") filled with synthetic seawater ("Instant Ocean").® Waste samples of various types and sizes were dropped from a plastic container which had a removable sliding bottom. The container was fitted with side extensions which enabled the device to hang such that the sliding bottom was immersed in the water column. Turbulence in the water column was achieved by using a steel screen (9" x 9", 1/4" mesh) mounted on a rigid rod.

In the drops of some wastes, such as those from the direct lime processes, the cohesion effects dominated. When released into the water column in the shape of a block, these wastes basically maintained their shape both as they fell to the bottom and immediately after contact. As they fell, individual particles of waste were continually eroded from the edges of the waste mass into the water column.

Other wastes, such as the gypsum, G1, and sulfite-rich dual alkali filter cakes (both as-received) exhibited much less cohesiveness. For these wastes a 200-gram sample, when dropped through the water column, broke up fairly quickly into 4 or 5 larger pieces and many small ones. During descent, surface erosion of the large pieces was observed to proceed at a faster rate than the surface erosion of the more cohesive lime waste samples. Consequently, for the dual alkali waste samples, approximately half of the sample reached the bottom as a semi-cohesive mass, the remainder as individual particles. The gypsum samples exhibited somewhat greater cohesiveness than the dual alkali material. It was observed that the individual particles of both materials exhibited a certain amount of density current behavior, i.e., they fell as a relatively large cloud whose fall velocity was greater than that of an individual waste particle. This cloud was observed to be "dirty" in that a large number of particles were left behind the cloud in the water column as the cloud fell.

The presence of this large cloud resulted in suspended solids levels after the dual alkali material drops that were greater than those accompanying the drops of the other, more cohesive wastes. It was also observed that the waste cloud associated with the apparently less cohesive materials was much larger in volume than that associated with the more cohesive materials. In some cases the walls of the test tank interfered with the further spread of the cloud, thus influencing (raising) the resultant suspended solids concentrations.

The fall behavior of these wastes was not only influenced by the type of waste dropped, but by the water content of that waste. This effect was most noticeable in the dual alkali sample. When dropped as-received, at 54% solids, this sample eroded quickly into the water column. When rewetted to a water content of 50%, however, another sample of the same material seemed much more cohesive and suspended solids levels in the tank were reduced by 30-40%.

(3) Modeling to Field-Scale Conditions

During the laboratory drop tests, qualitative observations were made of the nature of the descent of the waste to the bottom. The items observed included the propensity of the waste to break up, the extent of surface erosion (ablation) from the larger pieces as they fell, and the size and movement of the associated waste plume or cloud. Additionally, quantiative measurements were made of the suspended solids levels in the plume approximately 30 seconds after the drop and the suspended solids levels in midtank at intervals of 1 to 3 minutes. Finally, many of the waste drops were recorded on motion picture film. Thus, a good working knowledge of the behavior of various FGC wastes when dropped in 20 to 200 g lumps into a laboratory tank has been obtained.

Information gained in the laboratory can help to make predictions concerning typical barge drops of 3,000 m^3 of waste material into the ocean environment. However, the extreme differences between the field situation and the laboratory situations and the relative dearth of actual and theoretical knowledge concerning both the short-term transport phases of an ocean dump and the physical properties of the various wastes make direct correlations extremely difficult.

In the field, as in the laboratory, the behavior of the dropped waste would be determined by both the waste properties and the ambient water conditions. In particular, both the cohesiveness of the material (either apparent or true) and the extent to which it behaves as a density current when dumped will strongly influence the suspended solids levels and the distribution of the waste. In trying to incorporate these effects within a mathematical model, two basic problems in modeling field-scale drops are encountered: (1) determining the characteristics of the falling waste pieces, and (2) determining whether a density current effect (as opposed to individual particle fall) will dominate. These problems are discussed in detail below.

Characteristics of the Falling Waste Masses

In the laboratory experiments it was observed that 20-gram samples of certain wastes fell as one lump when dropped through a 3-foot water column. When the sample size was increased to 200 grams, some wastes broke up into half a dozen or more pieces as they fell, whereas others continued to remain intact. If an entire barge load of material were to fall intact to the bottom, the only material remaining in the water column would be that eroded from the surface of this block. This mass of suspended waste would be minimal compared to that found if the barge load had immediately (or eventually) broken into many smaller pieces during descent. Consequently, it is important to determine the approximate size distribution of waste pieces that occurs during an actual barge drop. This problem is an extremely complex one. The forces acting on a waste mass as it drops include both pressure forces and shear stress forces varying both spatially and with time in an unknown manner and strongly dependent on the ambient water conditions.

The reaction of the waste mass to these forces (with regard to breakage) is determined by its physical properties, primarily its shear strength. Knowledge of both the flow field in a drop and the physical properties of FGC wastes is limited, and the actual modeling of the breakage of a waste mass is complex. Furthermore, at this time the cohesive effects observed in certain wastes during the test drops cannot be conclusively explained.

Normally, a material exhibiting cohesiveness will have associated measurable soil properties known as Atterburg limits, including a plastic limit and a liquid limit. The liquid limit of a material is the minimum water content at which it behaves as a liquid as determined in a standard laboratory procedure. The plastic limit, similarly, is the minimum water content at which a material behaves in a plastic manner. In general, noncohesive materials such as coarse sand have no plastic limit; they never act as plastics. Cohesive materials such as clays, however, have both a plastic and a liquid limit. The numerical differences between these limits is known as the Plasticity Index and is a reflection of the physicochemical cohesivity of the material.

Few of the FGC wastes studied in the laboratory-scale bottom-dump barge simulations have shown a plastic limit. Dual alkali and gypsum wastes do not exhibit such a limit, while certain lime wastes do, according to work performed at the University of Louisville (3, 4). It is possible that these wastes without plastic limits exhibit relatively little true cohesiveness; even though the wastes tend to be fine-grained, they do not contain the clay minerals responsible for the cohesive behavior of naturally occurring soils.

It is also possible that apparent cohesion influenced the behavior of the FGC wastes during the bottom-dump barge simulations. This phenomenon can be induced in any fine-grained sediments, whether or not they exhibit true cohesion. All sediments, including FGC wastes, basically consist of a matrix of solid particles. The pore space between these particles is generally filled with either water or air. In a well-drained mass of sediment, one can observe a phreatic surface, that is, an elevation at which the pressure of the pore water is equal to atmospheric pressure. In coarse-grained sediments this surface generally separates the air-filled pore spaces from the water-filled pore spaces. In fine-grained sediments, however, the small interconnecting pore structure acts as a myriad of capillary tubes, and water is drawn up from the phreatic surface into the sediment. The height to which such water rises is a function of the sediment grain size and shape. When this phenomenon occurs, it increases the ability of the soil mass to resist shear along any surface, roughly by:

$$\Delta S = P_K \tan \phi;$$

where ΔS is the additional shear stress required for failure, ϕ is the internal friction angle of the sediment, and P_K is the induced capillary pressure, equal to the product of the unit weight of water and the height above the phreatic surface to which the water rises (5). This increased resistance to shear would increase the ability of a waste mass to maintain its integrity when dumped into turbulent water.

Apparent cohesion gradually dissipates when the sediment is immersed in water. This dissipation is expected, since the origin of the cohesive behavior is in surface tension, a phenomenon occurring at the air-water interface. However, due to the low permeability of fine-grained sediments, the dissipation of apparent cohesion may take a considerable amount of time and would initially be evident only at the edges of a waste mass. Without further work it is impossible to estimate accurately the appropriate dissipation times, although the low permeabilities for fine-grained sediments (approximately 10^{-4} cm/second) indicate that the apparent cohesion might likely be maintained even throughout a long waste drop (approximately 20 minutes), especially for larger pieces of waste. More theoretical and experimental work would be needed to determine the possible significance of apparent cohesion in determining the characteristic size of descending waste masses in long ocean drops.

In summary, determining the characteristic size of FGC waste masses that would be found in an actual waste drop is beyond present predictive capabilities. More work would be needed to determine the contributions of true cohesion, apparent cohesion, and turbulence in determining the characteristic sizes of waste masses in a field-scale drop.

Density Current Effects

It was observed in the laboratory experiments that the density current effect resulted in the clouds of individual FGC waste particles falling faster than the fall velocity of the same particles individually in still water. This effect has been observed in field drops of sewage sludge and dredged material (the latter with 70% water content) and is known to be extremely significant in decreasing the residence time of suspended solids in the upper water column.

The density current effect is found only when large numbers of relatively small particles are falling in close proximity. The key questions are: How many particles, how small must they be, and how close together? In Ocean Waste Disposal Practices (6) it is stated that suspensions with grain sizes less than 60 microns act as pure liquids and exhibit density current effects. In a field-scale FGC waste drop, however, it is conceivable that much of the waste might fall as 10-100 cm^3 pieces. At this point in time it is not known whether such a drop would exhibit density current behavior under typical ambient ocean conditions. More work in this area would be required to model reliably the fall of any mass of waste particles through the water column.

Present Theoretical Models and Modeling Results

There are mathematic models that attempt to describe the fall of barge-dumped material through the water column. Of these, the Koh-Chang model (7) is capable of accounting for a variety of conditions including density stratification and ambient horizontal currents. In this model the dumped material is assumed to consist of two phases, a solid phase characterized by constituents with various densities and fall velocities and a liquid phase. When dumped, the relatively dense mixture is assumed to fall as a hemispherical cloud under the action of gravity. As it falls, the cloud entrains ambient water and expands in volume. Any solid constituents whose fall velocities are greater than the fall velocity of the entire cloud are modeled as settling out of the cloud. When the waste cloud either reaches a neutrally buoyant position or encounters the bottom, it enters the collapse phase.

The Koh-Chang model assumes that the dumped material falls as a density current. Furthermore, the primary physical processes accompanying the fall of a cohesive material are ignored. These are the breakup of large masses and the phenomenon of surface erosion. Thus, although this model can be extremely useful and is fairly complete, it has limited applicability to FGC wastes.

The Koh-Chang model had only been validated in the laboratory for drops of noncohesive waste materials with relatively high water contents--a silty mud, digested sewage sludge, dredged material consisting of fine sand, and a salt solution. It is important that there was no field validation of this model; in the above-mentioned laboratory programs the drop size ranged from 0.7 cm^3 to 9 cm^3.

The applicability of the Koh-Chang model to FGC wastes is questionable due to the cohesion of these materials as observed in the laboratory drops. Therefore, using the results of the laboratory tests, a simple mathematical model not requiring a computer was developed to account for these cohesion effects. The major shortcoming of this simple model is that density current effects are neglected. A major new modeling effort would be required to account for both cohesion and other important effects.

Unfortunately, this new model is extremely sensitive to one of the less well quantified input parameters--the size of characteristic waste masses. Therefore, at best this model can obtain a wide range of possible suspended solids levels accompanying a given drop. However, the model is believed to use a valid approach, is applicable in situations where the assumptions of the Koh-Chang model are not, and gives insight into the falls of cohesive waste materials. Since this model ignores density current effects, it is most applicable when the convective descent phase is characterized by the fall of relatively few, large-sized masses of high cohesiveness and low erodability. The FGC wastes meeting these criteria would include those lime and limestone process materials tested in the laboratory-scale drops and would not include the dual alkali and gypsum materials.

The simple model focuses on the rate at which waste material is eroded from the surface of a cohesive mass as it falls through the water column. The basic characteristics of the model are outlined below.

- Overall Model Description--The model assumes that the dumped waste material enters the water as a predetermined number of roughly spherical pieces of a predetermined characteristic size. As these pieces descend through the water column, they are assumed to experience surface erosion only, with no further motion. The resultant suspended solids levels are determined by the concentration of eroded materials predicted at each depth.

- Engineering Assumptions--The rate at which material is eroded from a mass is assumed to be proportional to the surface area of that mass and to the square of the fall velocity of the mass. The constant of proportionality is a property of the individual waste and its water content and was determined for this effort from the laboratory drop test measurements. The eroded material is assumed to be left behind the falling mass as a plume whose cross-sectional area is assumed to be approximately 3.5 times the cross-sectional area of the dumped material in toto, as was often observed in the laboratory.

- Critique of Assumptions--The predicted suspended solids levels are relatively sensitive to the assumption that the cross-sectional area of the plume is 3.5 times the surface area of the barge. It is unlikely that the plume will be smaller than this. However, field observations of plumes in the New York Bight (8) of materials less cohesive than the FGC wastes examined in this program indicate that the cross section of some plumes might be ten times the surface area of the barge or greater. Since the predicted suspended solids levels are indirectly proportional to the cross-sectional area of the plume, this larger plume would result in suspended solids levels approximately one-third or less those presently predicted by the model.

  It is unknown at this time how sensitive the model is to the assumption that the erosion rate is proportional to the fall velocity squared. Erosion rates of materials are sometimes proportional to the cube or an even higher power of the relative velocity (9). If a higher power law were applicable, increased suspended solids levels and decreased penetration depths would be predicted for the larger sized (>200 cm^3) waste masses. A major consequence of the assumptions utilized in this model is that the mass of suspended solids resulting from the concurrent fall of several waste pieces is equivalent to the sum of the masses that would result from their independent falls. This assumption ignores any density current effects and thus invalidates the model for cases where this effect predominates. Since density current effects were observed in the laboratory drop tests of the various wastes, caution is implied in interpreting the model results.

- Results--The results of this model, as applied to various FGC wastes for a variety of potential sizes of waste masses, are summarized in Table IV-2. Although the model is capable of predicting average suspended solids levels throughout the water column as a function of depth, only the maximum suspended solids

TABLE IV-2

MODEL PREDICTIONS OF SUSPENDED SOLIDS LEVELS ASSOCIATED WITH DUMPED FGC WASTES

Waste Type	Assumed Size of Waste Masses	Z_{90}[a] (meters)	t_{90}[b] (minutes)	Predicted Maximum Suspended Solids Levels[c]	Engineering Estimate of Maximum Suspended Solids Levels
direct lime filter cake, w/o flyash 52% solids.	200 cc	100	3.9	15,000 ppm	100-10,000 ppm
	10^4 cc	200	3.3	7,500 ppm	
	10^6 cc => $1m^3$	330	2.2	4,600 ppm	
	3×10^8 cc => 10 pieces	860	2.2	180 ppm	
	3×10^9 cc => whole barge	1260	2.2	120 ppm	
direct lime centrifuge cake, w/flyash, 66% solids.	200 cc	> 500	>19.8	<3,700 ppm	100-2,000 ppm
	10^4 cc	>1000	>17.0	<1,850 ppm	
	10^6 cc => $1m^3$	>1700	>11.3	<1,150 ppm	
	3×10^8 cc => 10 pieces	>4460	>11.3	< 450 ppm	
	3×10^9 cc => whole barge	>8500	>11.3	< 300 ppm	
Dual Alkali w/o flyash, rewetted to 50% solids.	200 cc	18	.7	90,000 ppm	>1,000 ppm (outside range of model)
	10^4 cc	30	.6	45,000 ppm	
	10^6 cc => $1m^3$	60	.4	27,600 ppm	
	3×10^8 cc => 10 pieces	40	.4	1,080 ppm	
	3×10^9 cc => whole barge	210	.4	720 ppm	
direct lime 50% solids	200 cc	50	1.9	30,000 ppm	100-20,000 ppm
	10^4 cc	100	1.6	5,000 ppm	
	10^6 cc => $1m^3$	180	1.1	9,200 ppm	
	3×10^8 cc => 10 pieces	430	1.1	360 ppm	
	3×10^9 cc => whole barge	630	1.1	240 ppm	
Dual Alkali w/o flyash, (as received) 54% solids	4 cc	6	.4	243,000 ppm	Outside range of model
	60 cc	10	.5	159,000 ppm	
	10^3 cc	30	.5	76,400 ppm	
	10^6 cc => $1m^3$	75	.5	19,200 ppm	
	3×10^9 cc => whole barge	280	.5	5,100 ppm	

[a] Approximate depth to which 90% of the dumped sludge is predicted to descend as cohesive masses, leaving 10% suspended as fine particles in the water column. If the depth of water is greater than $3Z_{90}$ (approximately), the model predicts that all the sludge will be left suspended in the water column as fine particles.

[b] The time it takes for the sludge material still falling as lumps to reach Z_{90}.

[c] Always occurring at the surface in this model.

SOURCE: Arthur D. Little, Inc. estimates.

level in the water column is presented in the table. As discussed above, the erosion rate is assumed to be roughly proportional to the exposed surface area of the falling waste pieces. Furthermore, based on the assumptions outlined above, this exposed surface is at a maximum immediately following the dump before any erosion has occurred. Therefore, the model predicts that the maximum suspended solids level in the water column occurs immediately under the barge. This prediction is considered to be an artifact of the model, although in the absence of a density current effect, the maximum concentrations would indeed be expected to occur high in the water column.

The depth to which 90% of the waste material is predicted to fall as a cohesive mass, leaving 10% in the water column, is listed in Table IV-2 as Z_{90}. The maximum predicted depth to which cohesive waste pieces descend before entirely eroding away is approximately three times Z_{90}.

In preparing Table IV-2, engineering judgment was used to determine a range of reasonable sizes of waste masses for a given waste. A corresponding engineering estimate of the maximum suspended solids level accompanying a dump was then made, when possible. This estimate incorporates uncertainties in a variety of parameters, e.g., the waste mass size, the cross-sectional areas of the plume, and the rates of erosion. Estimates were unobtainable when the expected masses were small (less than 200 cm^3), as was the case for the dual alkali process materials and gypsum wastes. In ocean dumps of these wastes, density current effects, ignored in the model, are expected to be significant.

The range in suspended solids levels predicted for the more cohesive wastes encompasses two orders of magnitude (200-30,000 ppm). Greater accuracy in this estimate cannot be obtained without further theoretical or experimental knowledge of waste breakup in field-scale drops. A more extensive modeling effort, accompanied by a larger scale waste drop experiments would greatly increase the accuracy of these predictions and thereby contribute to the accurate definition of mixing zones for the case-by-case review of ocean dumping permit applications.

(4) Environmental Effects

The initial assessment identified a variety of adverse impact potentials associated with high levels of suspended sediment in the water column. Further, it was implied that corresponding levels of suspended FGC waste material because of their particle size and chemical composition (i.e., the presence of sulfite and trace contaminant fractions in some waste) could induce adverse impacts upon sensitive receptors in the planktonic and nektonic communities. The results of this assessment generally tend to deemphasize the potential for such adverse impacts in the upper reaches of the water column but leave open the question of their severity in the near-bottom environment subject to mud flows.

The results of the drop tests conducted at Arthur D. Little, Inc. indicate that at the laboratory scale the concentrations of suspended solids in the aftermath of drops of all types of the tested FGC material would be too small to engender the type of adverse impingement/anoxia results observed with higher concentrations of other sediments in the presence of sensitive juvenile finfish. In fact, concentrations at the upper end of the range observed in the drop tests would require exposure times of longer duration than those expected in order to produce measurable impacts even among the most sensitive finfish for which data are available (1).

Two principal uncertainties serve as qualifiers on the laboratory-scale results. First, the extent to which the resultant suspended solids concentrations observed at the laboratory scale reflect potential concentrations at field scale is still largely speculative. The predicted maximum suspended solids levels at field scale shown in Table IV-2 are sufficiently high so as to fall into the range expected to cause adverse impacts to a variety of representative organisms upon 24-hour exposure (1). The determination of 96-hour LC_{50} concentrations for suspended FGC wastes in the forthcoming test program is being designed to greatly narrow the range of uncertainty about this impact potential. However, it will not solve the problem of the absence of actual knowledge of field-scale suspended solids concentrations and exposure times.

The second major qualifying factor in the interpretation of water column impact potentials is the influence of the chemical transformations of sulfite-rich wastes during descent. This subject is discussed in more detail later in this chapter.

c. Long-Term Physical Fate and Effects of Untreated FGC Waste

(1) General Description of Long-Term Fate Processes

When a barge load of FGC waste is dumped into the ocean, it is expected to fall through the water column as described above. When the short-term transport process is completed, a certain percentage of waste may lie as a mass on the ocean bottom; the remainder will be distributed throughout the water column. Long-term transport processes, which would have already begun, now would take over. These processes include the dissolution and/or dispersion of suspended material and the flow, erosion, and/or dissolution of bottom deposits.

Both suspended and dissolved waste would be subject to dispersion and may be carried many hundreds of miles in the water column. The ultimate fate of the waste in the water column would strongly depend on the nature of the currents found in the disposal area.

The material on the ocean bottom would also be subject to movement. Under the force of gravity, a highly concentrated layer of suspended waste known as "fluff," "slush," or "fluid mud" will tend to flow as mud flow (defined below). Eventually, if not further influenced by water motion, this layer will settle and consolidate, and the mud flow will cease. The consolidation time will increase with the depth of the "mud" layer and the water content of the material and will be affected by any disturbance of the layer.

Waste deposited on the bottom could undergo erosion under the action of currents or wind-driven waves in addition to being subject to mud flow. Furthermore, eroded waste material may be resuspended into the water column. Depending on the nature of the waste and the ambient ocean environment, erosion may occur anywhere between the extremes of being continual or extremely sporadic, occurring only during intense storms. If the eroded material is composed of fine particles, then it would generally travel as suspended load in the water colum; if large flakes of waste erode, then bed load travel would probably prevail. The turbidity cloud associated with the erosion and resuspension of bottom deposits may be large in volume and may create high suspended solids levels. The height of water column affected by the resuspension of the waste may also be great if large-scale turbulence is present. Density stratification, on the other hand, would tend to restrict suspended sediments to a well-defined bottom layer.

Another process requiring consideration is the long-term transport of FGC waste in solution. The rate of FGC waste dissolution is closely related to the other long-term transport processes. For example, the dissolution rate of waste in a mud layer will almost certainly be less than the dissolution rate of waste particles suspended higher in the water column.

(2) Background Studies and Related Theoretical Work

Mud Flow

Mud flow is defined as the movement of a semi-liquid, unconsolidated layer of bottom sediment as a density current, generally under the action of gravity. In dredged material mud flows, sediment concentrations as high as 220,000 mg/l, equivalent to 19% solids, have been observed. At these concentrations, the sediment compacts very slowly, and the upward movement of water is hampered by the sediment matrix. Thus, a fluff layer may exist near the bottom for relatively long periods of time. An apparent fluff layer associated with a direct limestone scrubber waste discharge to a shallow marine embayment near Key West, Florida was observed to be in existence some 10 months after the reported occurrence of the discharge.

Observations of dredging and dredged material disposal operations (10) have convinced some researchers that the fluff layer phenomenon occurs only when the majority of the settling sediment particles are extremely fine-grained, in the clay or fine silt range. Masch and Espey reported in 1967 (11) that fluff layers were not found accompanying the dredging of silt or sand-sized particles.

The movement of disposed waste material by mud flow can be of major importance. Bassi and Basco reported in 1974 (12) that immediately following a dredged material dump consisting of a large percentage of fine particles, approximately 40% of the dredged material left the disposal area and spread out over the bay floor as mud flow. Six months after disposal the material covered an area three times the size of the original zone of deposition.

Mud flow behavior has been observed in laboratory-scale tests with some of the FGC wastes investigated, particularly wastes from direct lime systems. In view of observations of dredged materials, it is expected that FGC wastes with a high percentage of fine particles will exhibit this behavior to a larger degree than other wastes. (Most FGC wastes have a high percentage of fine particles in the silt-clay range.) Since wastes undergoing mud flow would be acting as liquids, it is expected that procedures used to facilitate waste handling by pumping (e.g., increasing water content) would increase the tendency of a waste to exhibit mud flow.

Erosion and Resuspension

Natural Environments

In general, wind-generated waves appear to have the greatest potential for causing resuspension of deposited materials on the ocean floor. Once in suspension, the material can be transported by even the smallest current. Consequently, in determining the likelihood of erosion, it is essential to consider the wave climate at the disposal site.

For deep water the maximum wave-induced water velocity is given approximately by:

$$V = \frac{2\pi a}{T} e^{-\frac{4\pi^2 z}{gT^2}}; \text{ valid when } \frac{2\pi z}{gT^2} > .5$$

where g is the acceleration of gravity, T is the wave period, a is the wave amplitude, and z is the depth (13). Thus, the magnitude of the near-bottom water velocity caused by wave action decreases exponentially with depth, with the longer period storm waves having a greater depth of penetration.

In general, the erosion-causing force (shear stress) exerted on bottom deposits is proportional to the bottom velocity squared. The detailed methodology for determining the magnitude of this bottom shear force may be found in Madsen and Grant (14). The constant of proportionality is also a function of wave period and increases with higher wave frequencies. By judiciously choosing a disposal site for its mild wave climate or great depth, one can, if desired, greatly improve the stability of the dumped material. Although other currents associated with oceanic circulation can also cause erosion, they are generally only responsible for moving material that has been resuspended by wave action (15). A detailed analysis of ocean currents near any dump site is essential to determine the direction and extent of movement that can be expected for a given waste material.

The long-term movement of waste materials through erosion, resuspension, and redeposition has been documented many times in the literature. Unfortunately, little or no field data exists on the erosion of ocean bottom deposits of wastes similar in nature to FGC wastes. Most of the data available is generally for the long-term movement of dredged materials, and most of the dredged material disposal sites monitored were located in shallow bays. At such sites, surface waves and tidal currents can periodically establish high-energy environments rarely, if ever, found on much of the continental shelf or in the deep ocean. However, examination of dredged material behavior at these shallow water sites provides insight into the behavior of ocean-dumped waste material in general.

Researchers investigating the behavior of dredged material disposal at shallow-water sites have noted the high mobility of the material at those locations. In 1962, Hellier and Kornicker (16) reported dredged material deposition 1-1/2 miles from a disposal site in relatively shallow Redfish Bay, Texas. A similar study was conducted by Nittrouer and Sternberg in 1975 (17) on the long-term fate of fine-grained dredged sediments dumped in a large tidal channel in Puget Sound. These sediments had a median grain size of .014-.030 mm, similar to grain sizes observed in FGC wastes. The disposal area was a high-energy environment; surface velocities of 110 cm/second were observed, as were velocities of 50 cm/second in the lower regions of the water column. Four months after disposal approximately 80% of the dredged material had been eroded and transported from the disposal site. Primarily fine material had been selectively removed, while the sediments remaining in place had consolidated enough to resist further erosion. This type of "selective erosion" has also been reported by other observers (18, 19).

The turbidity plumes that accompany the resuspension of bottom deposits of waste materials may be of considerable extent and concentrations (e.g., thousands of ppm) (11). In addition, similar turbidity plumes may result from the resuspension of naturally occurring materials.

However, physical properties of dredged materials vary greatly as do ambient ocean conditions among disposal sites. Rarely have these variations been well documented. Thus, it is difficult to generalize about the mobility of dredged materials or make accurate predictions that would apply to FGC waste or even dredged materials in other situations.

Laboratory Studies of Natural Sediments

Due to the regular lack of documentation of certain pertinent conditions in the field, laboratory studies have been frequently more valuable as predictive tools in determining the mobility of bottom deposits of sediment-like material. Laboratory studies have indicated that the behavior of any given sediment with respect to erosion is a property of the local shear stress applied to the surface of that material by the flow above it. To each sediment there corresponds a "critical shear stress," t_c. When the applied shear stress is less than t_c, no erosion occurs. In such cases, the entraining force exerted by the fluid is not great enough to overcome the combined effects of the inertia of the sediment particle, the friction force between adjacent sediment grains and the cohesion (true or apparent) of the material. At applied shear stresses greater than t_c, erosion of the bottom sediment will occur. The rate of erosion is usually measured as depth of material removed per unit time, or mass of material removed per unit surface per unit time. Theoretically, for a given bottom sediment, the rate of erosion will be a function only of the shear stress applied to the sediment by the water flow above and around it.

Experimentally measured erosion rates or critical shear stress values are rarely reproducible with precision. In general, these values can be expected to vary by a factor of two or even three. This is due to the complexity of the erosion phenomenon and the difficulty of setting up precisely reproducible experimental conditions. In many cases, determining the onset of erosion is largely subjective, since erosion rates at the involved shear stresses are extremely low. Furthermore, these experiments are never exactly reproducible since erosion initially occurs near small irregularities in the bottom surface where shear stresses are locally high. Whereas, theoretically, an erosion rate for a given material is constant in the absence of deposition of suspended materials from the flow, erosion rates in the laboratory have been observed to decrease during the course of the experiment. This effect is due to the variation of physicochemical properties with sediment depth. The top layer of sediment initially exposed to the water surface may have a high water content and be easily eroded. More consolidated layers beneath this layer may erode at far slower rates under the same flow or not at all. Variations of erosional properties are seen over thicknesses of less than .5 centimeters of sediment material. Thus, for a given material, a wide range of critical shear stresses or erosion rates may be reported.

Many investigators have studied the variation of t_c and erosion rates with other, more easily measured physical properties including cohesiveness (as reflected in the plasticity index or clay content of a material), shear strength, degree of consolidation and particle size. These investigations are summarized in the 1975 Sedimentation Manual (9), edited by the American Society of Civil Engineers.

Many investigators have agreed that particle size is one of the more important influences on erosion properties. Studies of quartz particles of various sizes indicated that there is a range of particle sizes at which quartz sand is most easily eroded (7). This range is shown in Figure IV-2, along with the typical range of particle size distributions for FGC wastes (1). At finer particle sizes, cohesion caused the quartz sand to become more erosion-resistant. At larger particle sizes the inertia of each individual sand grain hindered mobility. These phenomena are observed for sediments other than quartz sand, although the actual range of particle sizes for maximum erosion may vary from material to material.

It has also been observed that increasing the percentage of fine, cohesive material such as clay in a sediment increases its erosion resistance. Researchers such as Smerdon and Beasley (20) have found that the critical shear stress t_c increases as either the plasticity index or clay content of a sediment is increased. Other physical parameters that have been studied did not have an easily discernible effect on the erosion behavior of a sediment, and the experimental results have been contradictory. For instance, Dunn (21) observed that consolidation increases the value of t_c for a variety of soils; Partheneides (22), however, observed that the consolidation of San Francisco Bay mud did not affect t_c at all, even though the shear strength of the sediment increased by three orders of magnitude. No relationship has been found between measured values of t_c and the unconfined compressive strength of a material (23).

(3) Laboratory Studies of FGC Wastes

Since the sediments investigated in the above-mentioned studies are naturally occurring, applying the results of the studies to an artificial material such as FGC waste might be considered questionable. However, the naturally occurring sediments studied (muds, sands, silts, and clays) showed a very wide variation of physical characteristics. In gross physical properties the FGC wastes are more similar to mud than is naturally occurring beach sand. Therefore, it is reasonable to assume that, ignoring considerations of FGC waste solubility, any relationship between erosion behavior and other physical properties that is found to hold true for the wide range of naturally occurring sediments will also at least temporarily hold true for FGC wastes.

Erosion experiments conducted at the New England Aquarium (NEA) have greatly expanded knowledge concerning the mobility of FGC wastes. These experiments, described in detail in Appendix B, were conducted in a large (1,400-liter) annular flume. A layer of FGC waste was placed on the bottom of a small section of the flume and the water circulated at predetermined velocities. Suspended solids levels in the water column were monitored, and the mass of waste eroded away was calculated by weighing the sample both before and after the experiment. In this manner the flow conditions required to initiate erosion of each sample were determined; under increased flow conditions the rates of erosion of the waste samples were calculated. From these results one can begin to make rough calculations

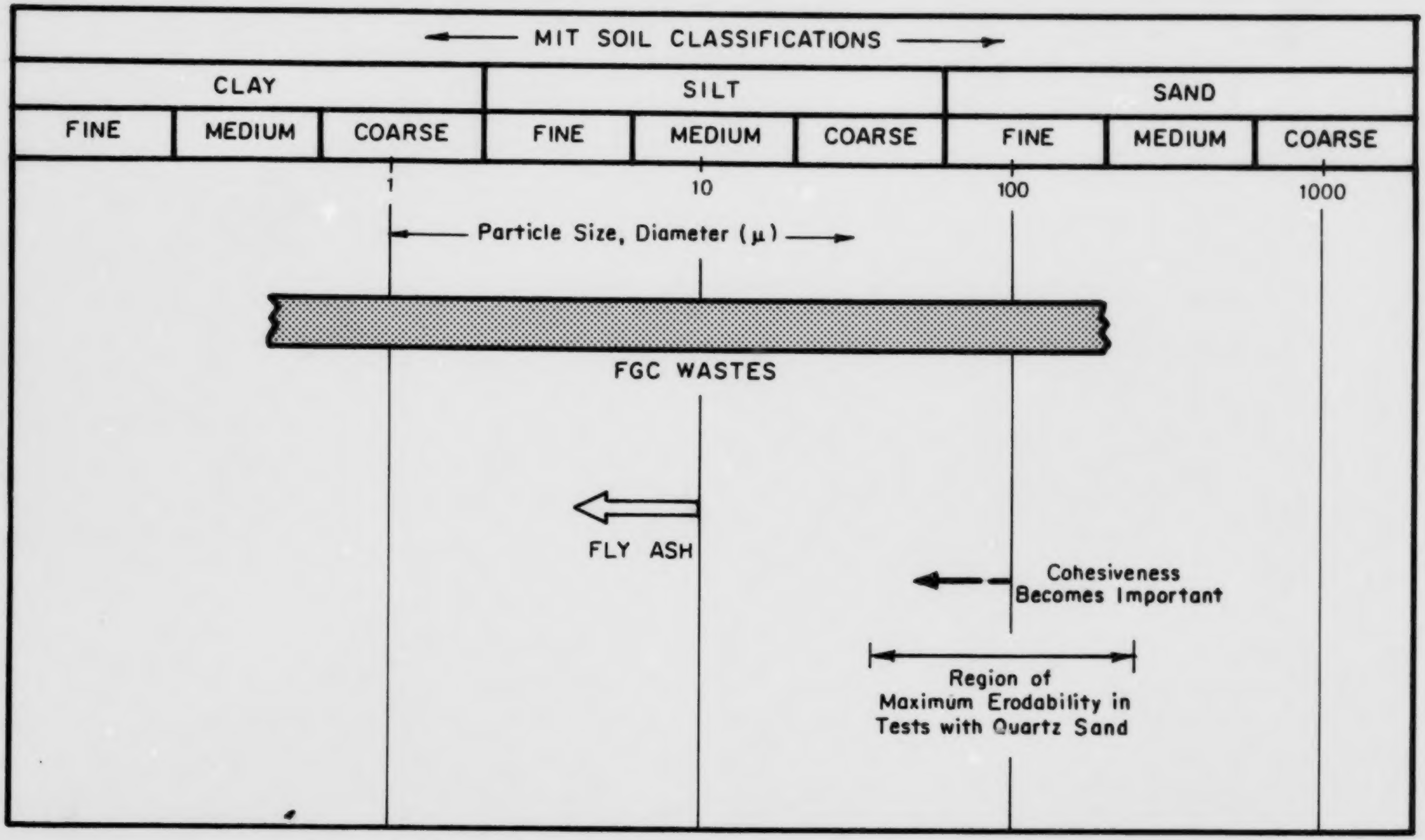

MIT SOIL CLASSIFICATIONS
CLAY
SILT
SAND
FINE
MEDIUM
COARSE
FINE
MEDIUM
COARSE
FINE
MEDIUM
COARSE
1
10
100
1000
Particle Size, Diameter (μ)
FGC WASTES
FLY ASH
Cohesiveness Becomes Important
Region of Maximum Erodability in Tests with Quartz Sand

FIGURE IV-2 COMPARISON OF PARTICLE SIZE RANGES OF FGC WASTES AND SOILS

Source: Arthur D. Little, Inc.

of the rate at which FGC waste will be removed from a disposal site if the flow conditions at the disposal site are known and the areal extent of the waste on the bottom has been determined. Of course, the accuracy of this determination depends on the extent to which temporal physicochemical changes in the waste and complex bottom topographies can be accounted for.

Onset of Erosion

Figure IV-3 presents a range of critical shear stress for a variety of materials including the FGC wastes tested as part of this program at NEA. It is clear that t_c can vary greatly from sediment to sediment. In general, the sediments that resist erosion most successfully are those that are so coarse-grained that they are difficult to move, such as coarse sand, or are extremely fine-grained and exhibit cohesion. (San Francisco Bay mud is a potentially puzzling exception to this generality.)

All the wastes tested appeared to be more erosion-resistant than the medium- and fine-grained sands in other experiments. However, the wastes were less erosion-resistant than some of the more cohesive materials such as Fall River dredged material, clay, and sand/clay mixtures. Of the three FGC wastes tested at the NEA, DA4 dual alkali waste, rewetted to a solids content of 52%, was the most easily eroded. The critical erosion velocity was determined to be less than 6 ft/second, with a critical velocity of approximately .75 ft/second.

While the onset of erosion is determined by the magnitude of the applied shear stress, two additional scales are provided in Figure IV-3 for measuring initiation of erosion. The velocity scale can be used to correlate the initiation of erosion with the velocity of a uniform flow just outside the near-bottom boundary layer. In a typical uniform flow, this near-bottom velocity may be approximately two-thirds of the velocity of the flow above the bottom (24). The wave amplitude scale can be used to correlate the initiation of erosion with the amplitude of a 10-second wave on the surface 100 feet above the bottom. These two comparative scales are accurate only if the bottom is hydraulically "smooth" (12). It is expected that this criterion would usually be satisfied for the finer-grained FGC wastes and for clays on a flat bottom. All three scales can be considered valid in determining the initiation of erosion of these materials. However, the velocity and wave amplitude scales are not valid for determining the onset of erosion of materials containing large particles (>.05 mm). For these materials, erosion will start at lesser water velocities and smaller wave amplitudes than those indicated on Figure IV-3.

When one compares current velocities that have been measured in the on-shelf environment with the results of the NEA tests, it seems clear that both current and wave action can be severe enough to cause the erosion of bottom deposits of even the more cohesive FGD wastes on a regular basis.

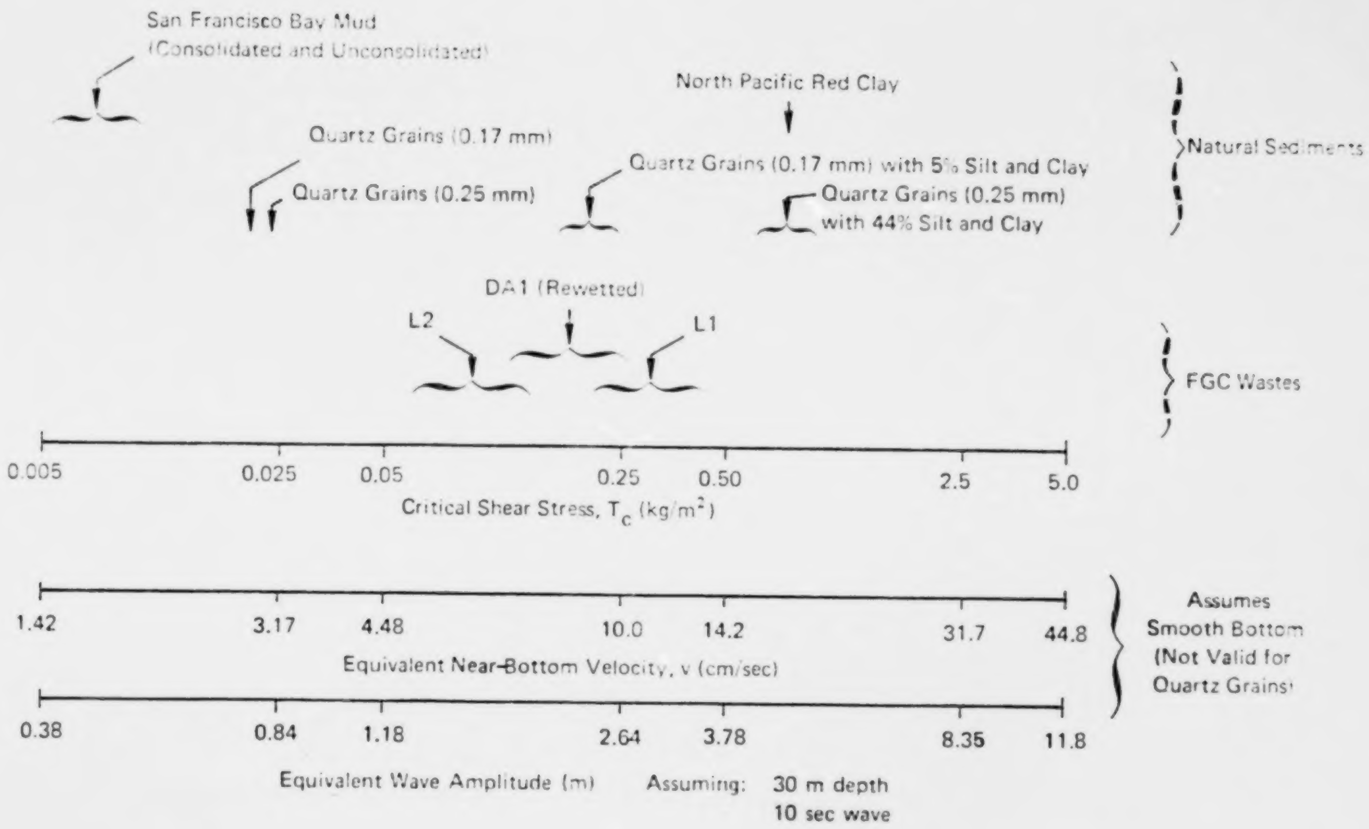


FIGURE IV-3 CRITICAL SHEAR STRESSES FOR NATURALLY OCCURRING SEDIMENTS AND FGC WASTES

Source: Arthur D. Little, Inc.

Erosion Rates

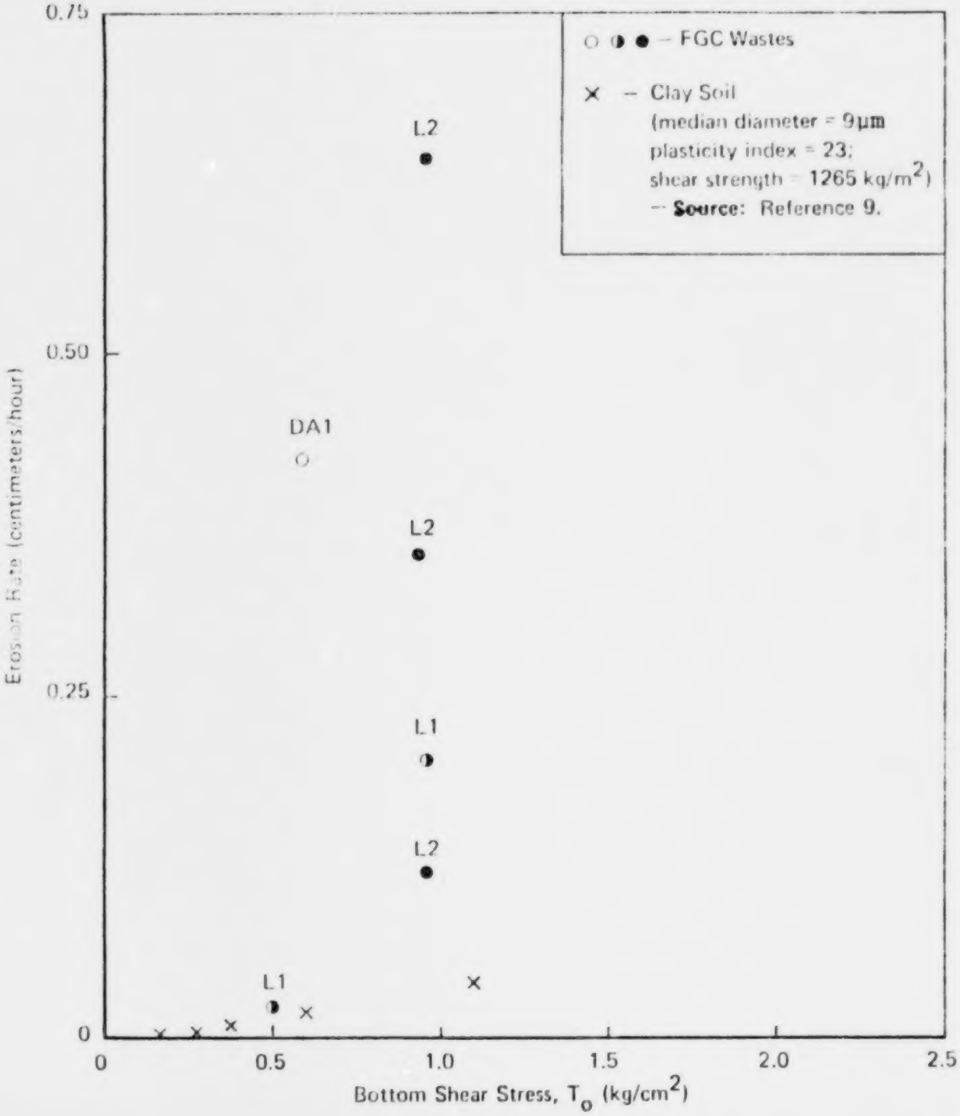
At applied shear stresses greater than its value of t_c a sediment will erode. The rate of erosion is a function of the applied shear stress and the sediment type. Figure IV-4 presents data representing the laboratory measured erosion rates of an extremely clayey soil and a variety of FGC wastes. The data are for the FGC wastes and dredged material in the NEA tests. The erosion rates are presented as a function of the applied shear stress. The rates presented for wastes and dredged material are considered accurate within no less than a factor of two to three. This inaccuracy is at least partly a direct result of the natural variation observed in erosion rates (see Appendix B). Even allowing for this margin of error, the erosion rates of the FGC wastes are greater than those of the clay soil or the dredged material under similar shear stresses. Of the FGC wastes tested, the dual alkali process sample was the most easily eroded, whereas the direct lime process wastes were more erosion-resistant. These results parallel those presented in Figure IV-3; the dual alkali wastes tested had a lower critical shear stress than the two lime process wastes. These erosion test results are also consistent with the results of the laboratory drop tests. In the laboratory-scale drop tests a high erosion rate was observed during the drops of the dual alkali wastes. The direct lime wastes, on the other hand, experienced relatively minor surface ablation during descent through the water column.

Manner of Erosion

Eroded material that moves as suspended load may be carried far from a disposal site by current. Eroded material moving as bedload, bouncing along the bottom, will rarely travel as far. Thus, by observing the manner in which eroded material is moved, one can begin to determine its range of potential impact.

During the erosion experiments conducted at the NEA, observations were made of the manner in which eroded FGC waste material was moved. All of waste was observed to undergo erosion through both flaking and streaming. The large flat bits of waste that flaked from the surface ranged in size from less than 1 sq. cm to 4-5 sq. cm and generally traveled as bedload. The largest flakes were observed during the testing of the DA4 dual alkali waste. Much of the material eroded from this sample seemed to travel as bedload.

Surface streaming, in which fine particles were eroded continuously from the surface of the waste into the water column was also observed. This action predominated the erosion of the Fall River dredged material and the L1 and L2 lime wastes. Material eroded in this manner generally traveled as suspended load in the water column.



Sources: Reference 9 and Arthur D. Little, Inc.

FIGURE IV-4 EXPERIMENTAL OBSERVATIONS OF EROSION RATES FOR FGC WASTES AND CLAY IN SEAWATER

(4) Observations of FGC Waste Behavior in a Marine Environment (Key West, Florida)

During late 1974 and/or early 1975 an inadvertent discharge of FGC waste from a direct limestone scrubber system took place at the City of Key West's Stock Island Power Station. The discharge originated at an overflowing holding pond and reportedly flowed overland about .1 kilometers to a 16" storm drain where it entered a small marine embayment. The embayment is about 0.3 kilometers wide by 0.9 kilometers long, widening as it opens southward to the sea over broad (about 1.0 km^2), shallow (0-2 meters) coral reef area. The embayment is quite shallow except for a borrow pit in the northeast end and a marine channel and basin on the eastern side. The maximum depth in the marine channel is about 5-6 meters. A shallow (1-2 meters) ditch along the western margin was apparently dredged either for fill or to provide a channel for cooling water discharge into the bay. The FGC waste discharge entered this 15-20 meter wide ditch and apparently spread over a wide area before completely settling on the bottom. Much of the waste volume was apparently deposited within the confines of the ditch, but there was evidence of waste accumulation on the shallows beyond the ditch as well.

As part of this program the site was visited twice by staff of Arthur D. Little, Inc., once in October 1975 and once in December 1976. In October 1975 the water in the embayment was very turbid, and fine white material was found deposited on the adjacent mangrove flats and bottom detritus. Waste deposits were exposed at the sediment/water interface near the storm drain. The waste was very soft, offering little support and greatly impeding efforts to walk through it. It appeared to be over 0.5 meter thick in places.

In December, 1976, other sediments, primarily composed of coarse coral sand, had covered the waste deposits with a 3-8 cm thick layer of coarser material, and waste was no longer exposed directly to the water of the bay. Waste was not immediately apparent and was not a measurable sediment fraction in cores taken approximately 100 meters south of the discharge point. Immediately off the discharge point, cores showed a top layer of recent sediment (apparently washed into the ditch from the adjacent shallows) covering about 0.5 meter of the waste which overlay the pre-existing fine, crushed coral and sand sediments at the core bottom. The undisturbed waste bed in the ditch was still unconsolidated in December 1976, though more recent coarser material overlay it, substantially isolating it from the overlying waters. The mobility of the covered material is unknown. It seems possible that it may flow as a viscous liquid if it has not already accumulated in the lowest possible depressions.

In December 1976, two relatively homogeneous fist-sized masses of waste were retrieved from a depth of about 0.3-0.5 meter below the surface at a point adjacent to the origin of the discharge and placed on the bottom in water about 0.3 meter deep. They were observed and photographed over the period of one hour as the 8-15 cm waves and less than 5 cm/second current modified and redistributed them. Wave-induced periodic motion on the bottom was indicated by the 0.3-0.6 cm oscillations of suspended material and detritus. Initially, the waste samples were rather angular and stood some 8 cm above the bottom. Very early after placement (2-5 minutes), fractures appeared and slumping of the angular shoulders of the mounds occurred. This fracturing and slumping continued as long as the mounds remained angular; the larger chunks slumping first, then smaller chunks following in sequence as the mound profiles became lower and smoother.

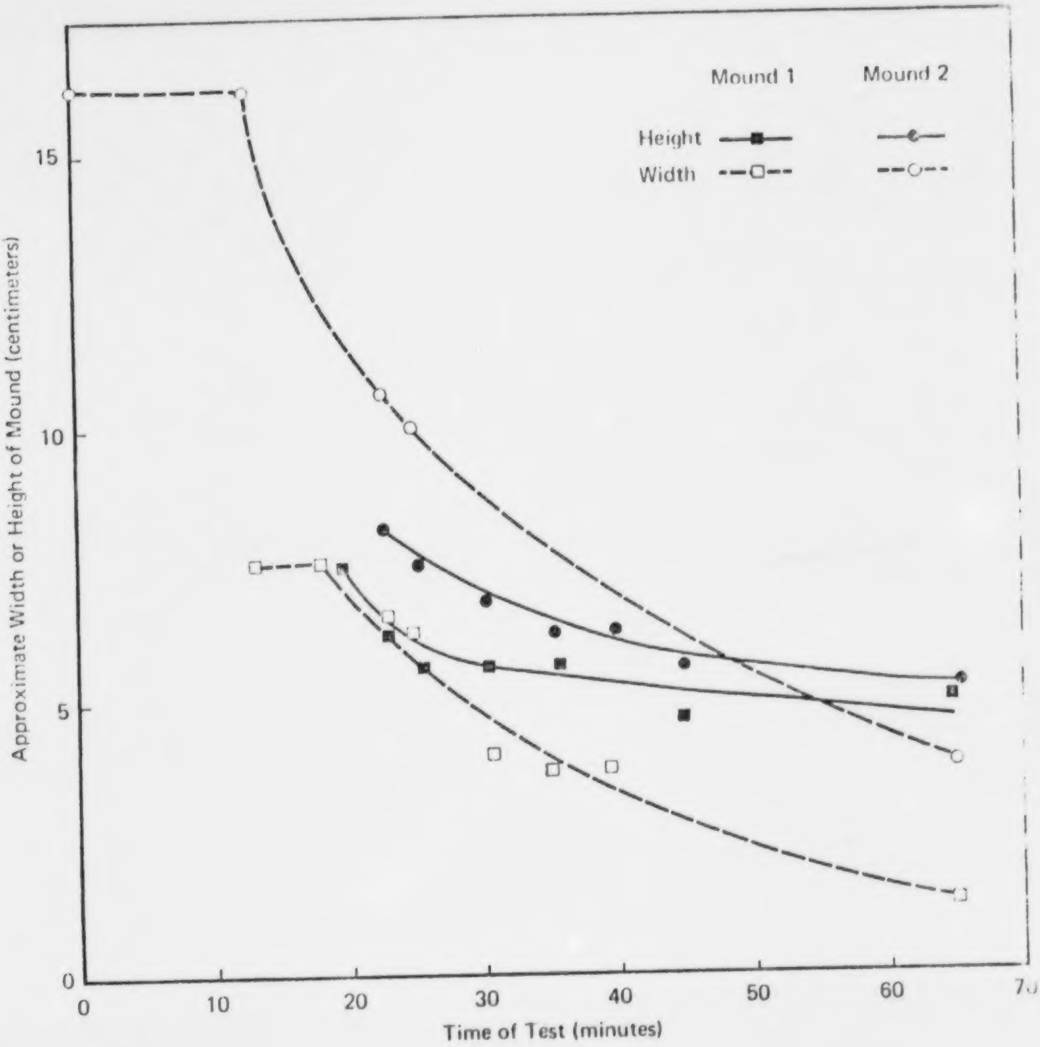
The one-hour long transformation of the angular shaped masses of waste to low-profiled mounds is plotted in terms of mound height and ridge crest length in Figure IV-5. Calculations assuming simple, regular-shaped geometries have shown that the volume of each mound was reduced by about 30% by erosion during the experiment. Though there is unevaluated experimental error in determining the mound height and width and no attempt was made to estimate the amount of sediment spread beyond the apparent base of the waste mounds, it is clear that this type of waste will be highly mobile when deposited in lumps on the bottom and subjected to minor currents and oscillatory water motion. Waste resuspended by erosion was observed much of the time in the field and appears in many of the photographs. It is estimated that a great deal of the resuspended sediment was carried beyond the camera's field of view under the conditions prevalent during the experiment. Even allowing for unnoticed resettling of sediments in the immediate vicinity of the mounds and possible errors in mound height determinations, it is conservatively estimated that at least 20% of each of the original mounds were eroded and transported away within one hour.

(5) Summary Considerations of Long-Term Physical Fate

Several particular FGC waste have now been studied in greater detail in laboratory experiments. These include:

- L1 direct lime centrifuge cake with fly ash (as-received);
- L2 direct lime filter cake without fly ash (as-received); and
- DA4 dual alkali, rewetted to a solids content of 52%.

A basic qualitative comparison of the erosion-related properties of these wastes with those of a dredged material (Fall River mud) is presented in Appendix B. In general, these wastes were all observed to move as mud flows and were observed to be eroded and suspended under flow conditions commonly found in the ambient ocean environment. These wastes all exhibited greater mobility than the dredged material.



Source: Arthur D. Little, Inc.

FIGURE IV-5 OBSERVATIONS OF MOUNDS OF FGC WASTES CREATED IN SHALLOW WATER ENVIRONMENT

Figures IV-3 and IV-4 showed the critical shear stresses present at the onset of erosion in the laboratory and the measured rates of erosion under certain flow conditions. These numbers are considered to be accurate within no less than a factor of two to three, primarily due to natural variation rather than experimental error. If flow conditions are known and time variations of waste properties are ignored, then the erosion rates given can be used to determine the maximum rate at which waste would be removed from a disposal site through erosion.* The distance such eroded waste material would travel or the rate at which it would travel under given flow conditions cannot be determined at this time. In general, however, waste moving as suspended load would travel farther and faster than waste moving as bedload.

It is difficult to assess the influence of variations in waste properties such as water or fly ash content on erosion properties. Extensive study of this subject with naturally occurring sediments has met with limited success. It is tentatively suggested that the propensity for FGC waste mud flow could be increased with increasing water content and fly ash content; although, based on laboratory testing to date, no firm conclusions can be drawn. Water content is thought to be significant, with the less consolidated wastes of higher water content exhibiting a propensity for erosion. This behavior has been observed in naturally occurring sediments, although exceptions exist (9).

In using the laboratory test results (shown in Figures IV-3 and IV-4) to predict waste movement in a field situation, several factors must be considered. First, the values presented in these figures could only be valid for wastes at the water contents studied. When deposited on the bottom, these wastes may either consolidate or swell, resulting in changes in their erosion properties.

After an hour's immersion in water, control samples of one of the lime wastes showed no radical change except spreading through mud flow. A control sample of DA5 dual alkali waste, however, was observed to swell appreciably. Therefore, this effect merits further consideration.

Second, the shape of a mound of deposited waste would be a significant factor in determining erodibility and erosion rates. In a given situation ambient ocean bottom conditions as measured before dumping may not be severe enough to lead one to predict erosion. However, the local shear stresses caused by current and/or wave action on an irregularly shaped waste mound might well be great enough to cause erosion. This phenomenon must be recognized when assessing the potential for long-term waste movement.

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*The rate of removal obtained in this manner is a maximum rate, since in large disposal areas, waste eroded from one section of the area may be redeposited on another section. Thus, not all eroded material necessarily leaves the disposal site.

Finally, the phenomena of chemical and biological fate, including dissolution, must be considered. These factors may contribute significantly to the occurrence and/or magnitude of long-term transport of ocean-dumped FGC wastes.

The results of field investigations of a shallow marine embayment receiving a waste discharge support and supplement the results obtained in the laboratory. Here, initial relatively widespread deposition of fine fractions appears to have taken place, followed by subsequent confinement of the bulk of the discharged material by deposition of coarser background sediments. The propensity of the unconfined waste fraction to erode was demonstrated by the reexposure of previously buried waste to the ambient currents on the bottom of the embayment.

The revisiting of the lagoon adjacent to the Stock Island power plant, discussed above, provided an extremely useful reference point concerning waste disposal in marine situations subject to subsequent deposition of "natural" sediments. When visited during the initial assessment, the area in the vicinity of the waste overflow was largely devoid of benthic macrofloral or macrofaunal organisms. The date of this visit is estimated to have been some nine to ten months following the cessation of the overflow. At the time of the visit made during this assessment some 23 months after the overflow, a different picture emerged. As noted above, redeposition of the relatively coarse coral sand, itself somewhat unstable but characteristic of many "control" locations in the embayment, had been followed by the reappearance of benthic macroorganisms. The area of the waste overflow was vegetated, albeit somewhat sparsely, with an as yet unidentified filamentous green algae. This species was also observed to characterize the remainder of the embayment in areas where the original turtlegass (*Thallasia*) community had been displaced, apparently by the combination of channelization and thermal effluent stress. Along with the revegetation, the consumer level in the marine food web was reestablished in the form of grazing gastropods tentatively identified as members of the genus *Marginella* or a closely linked species. The extent of vegetation and invertebrate colonization in the area of waste deposit and subsequent sediment redeposition did show an apparent correlation. That is, the density of organisms increased with distance from the locus of the overflow. However, this followed the general pattern of organism distribution versus water depth reflected in other apparently unaffected areas of embayment. Thus, cause and effect relationships based on the presence of the waste beneath the redeposited sand would be somewhat speculative.

The important finding in this investigation is that upon redeposition of suitable substrate there is nothing inherent in at least one type of FGC material that prevents recolonization by benthic flora and fauna. There are still many unresolved questions about this subject including the extent to which such recolonization might be precluded by benthic oxygen depletion and/or trace contaminant availability in association with FGC materials. The continuing testing program is aimed at answering some of those questions in even more extreme situations where the waste itself would serve as substrate.

The results of the erosion tests performed by the NEA, combined with the field observations off Stock Island, lead to verification of the first of the concerns about wastes in the benthic environment noted in the initial assessment. Specifically, the potential for mud flows of FGC materials seems to exceed that of comparable substances such as dredged material. Consequently, it still appears that under typical on-shelf ambient conditions, untreated FGC waste would not form a stable substrate suited to the development of a diverse benthic macrofaunal community. However, as apparent in the Stock Island situation, the waste can be deposited in quantities and at rates to form a substrate that permits colonization. This potential would exist in areas subject to limited mixing and flushing in the benthic environment. Many deep ocean (off-shelf) sites could fall into this category. Thus, it is important to determine the extent to which benthic accumulations of waste under relatively quiescent conditions serve to limit faunal utilization. Long-term exposure tests in the upcoming work program are being designed to reflect this.

It does not appear feasible to investigate the influence of mud flows of FGC wastes on benthic community development at the laboratory scale. However, at limited field scale, such investigations may be feasible.

In summary, benthic sedimentation impacts still appear to be a substantial concern for soil-like FGC material, but there is substantial evidence to support the expectation of benthic community establishment in situations where FGC materials become covered by the redeposition of suitable "natural" sediments.

2. Chemical Fate and Effects of Dissolution/Oxidation

a. Introduction

It is expected that the potential extent of sulfite-related impacts of ocean-dumped FGC materials is dependent principally upon the following factors: (1) chemical composition (sulfate/sulfite ratio, presence of fly ash, and dissolved sulfite in the occluded waste liquor); (2) physical properties (crystalline morphology, particle size distribution); and (3) the mode of disposal (dispersed versus concentrated dump, depth of disposal area, etc.). These factors would govern the availability of sulfite either as solid or dissolved fractions and the exposure of the waste material to the environment.

However, the concerns regarding sulfite toxicity and oxygen depletion identified in the initial assessment were largely hypothetical in light of the absence of empirical data on dissolution and oxidation rates of the FGC wastes. Laboratory studies were therefore undertaken on dissolution and subsequent oxidation of sulfite from untreated FGC wastes in order to provide some insight on sulfite-related impact issues and, to a less extent, the questions of trace contaminant availability also raised in the initial assessment.

b. Laboratory Observations

Laboratory experiments pertaining to sulfite-related impacts of untreated FGC wastes were performed in two areas:

- the rate of dissolution of sulfite and the equilibrium sulfite concentrations under anoxic conditions; and
- the dissolution of sulfite and potential for oxygen depletion of seawater.

The conditions of the tests conducted varied according to the specific effects being examined. In general, the experiments focused on two parameters: the suspended solids level (quantity of wastes); and the nature of the waste material. Five different untreated sulfite-rich materials were used as summarized below:

Type of System	Waste Designation	Type of Dewatering	Wt % Solids	Sulfite Content (mmols/dry gm)	Wt % Acid Insolubles
Dual Alkali	DA2	Filter	63	5.5	~0
	DA3	Filter	57	2.7	31
Direct Lime	L1	Centrifuge	63	3.8	35
	L2	Filter	52	5.8	1
	L3	Filter	47	5.9	3

The results of these tests are discussed briefly below. Details are presented in Appendix B.

(1) Dissolution Rate and Equilibrium Sulfite Concentrations

The maximum soluble sulfite concentration achieved in seawater will depend primarily on the solubility product of calcium sulfite (which is a function of ionic strength and temperature), the initial concentration of calcium in the seawater, and the nature of the waste itself (sulfate/sulfite ratio of calcium-sulfur salts and presence of soluble sulfite in occluded liquor). Similarly, the rate of dissolution of calcium sulfite solids can be affected by a number of factors including: the chemical composition and crystalline morphology of the solids; the physical state; temperature; and the variation from equilibrium concentrations.

Equilibrium solubility tests were run in deaerated synthetic seawater with an ionic strength of 0.652 mols/liter and a pH of 8.3 and containing about 390 ppm of calcium and 2,500 ppm of sulfate. The equilibrium concentration of sulfite achieved covered a range of $1.6\text{-}2.4 \times 10^{-3}$ mols/liter (130-190 ppm) for the different FGC materials tested at two temperature levels (15 ± 1°C and 21 ± 1°C). This sulfite concentration range represents about a fivefold stoichiometric excess over the concentration of oxygen in air-saturated seawater. The average apparent solubility product (K_{sp}) over the range of conditions was 2.8×10^{-5} $\text{mols}^2/\text{liter}^2$.

The temperature dependence of the solubility product could not be assessed, since differences in values obtained were within experimental error of measurement.

The increases measured in the concentration of calcium due to the dissolution of the FGC wastes was in every case larger than the quantity of sulfite dissolved by at least 50%, indicating the dissolution of other calcium salts from the wastes (e.g., calcium sulfate and calcium hydroxide). Under equivalent conditions the increase in calcium concentration was greater for the dual alkali wastes than for the direct lime wastes (and correspondingly, the increase in sulfite concentration for the dual alkali wastes was lower than that for the direct lime wastes).

The time required to achieve equilibrium also varied with the type of wastes. With fly ash-free wastes, dual alkali filter cake required almost three times longer than the direct lime filter cake to achieve 90% of the equilibrium sulfite concentration (approximately 40 minutes versus approximately 15 minutes) at an initial suspended solids level of approximately 3,000 ppm.

(2) Simultaneous Dissolution/Oxidation

Three different types of tests were run with both direct lime and dual alkali sulfite-rich wastes to investigate sulfite oxidation and simultaneous sulfite dissolution/oxidation:

- oxidation of sodium sulfite at dilute concentrations at synthetic seawater (1.8-12.8 x 10^{-4} M sulfite, with 3-4 and 6-8 ppm oxygen);
- simultaneous dissolution/oxidation experiments in agitated suspensions of waste solids in synthetic seawater at varying suspended solids concentrations (25,000-50,000 ppm waste in saturated-air seawater); and
- dissolution/oxidation studies in simulated drop tests to evaluate the effects of low levels of turbulence and degree of waste exposures.

The results of these experiments clearly indicate that the dissolution of sulfite will normally be the controlling factor in determining the extent of related oxygen depletion of seawater. The reaction of soluble sulfite with dissolved oxygen is complete within three minutes at sulfite concentrations in seawater of 1 x 10^{-4} M and greater. Figure IV-6 shows plots of oxygen consumption rates at varying sodium sulfite concentrations.

The rate of oxygen-depletion of seawater in tests with prewashed sulfite-rich wastes was very dependent upon the factors affecting the availability of sulfite, i.e., the suspended solids level of the seawater/waste slurry, the calcium sulfite content of waste, and the degree of agitation or

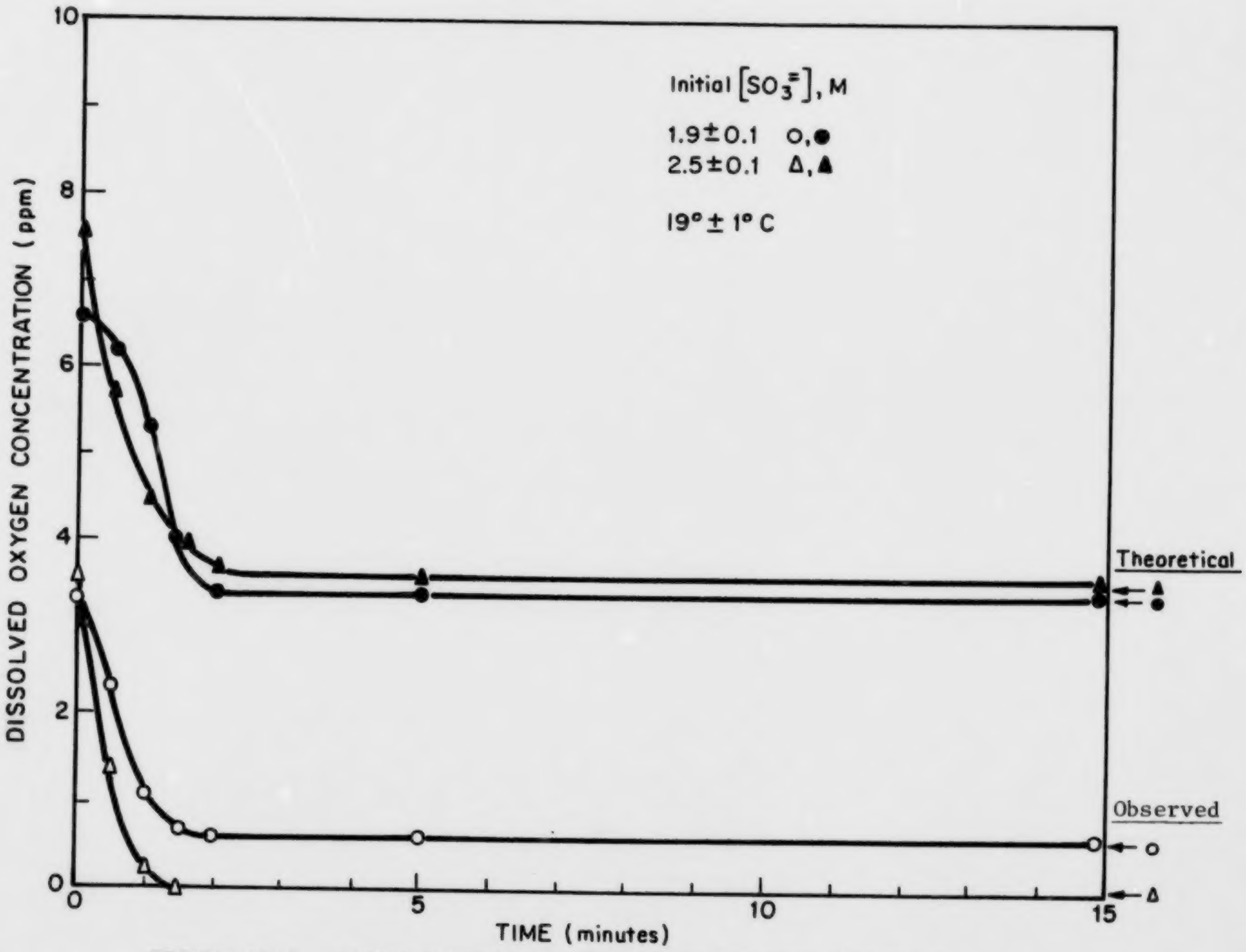


FIGURE IV-6 OXYGEN CONSUMPTION IN SODIUM SULFITE SOLUTIONS

Source: Arthur D. Little, Inc.

turbulence. Figure IV-7 shows the effects of slurry concentration on the rate of oxygen consumption using direct lime wastes (without fly ash) under highly agitated conditions, and Figure IV-8 illustrates the effects on the degree of oxygen depletion of differences in waste type and calcium sulfite content of the waste.

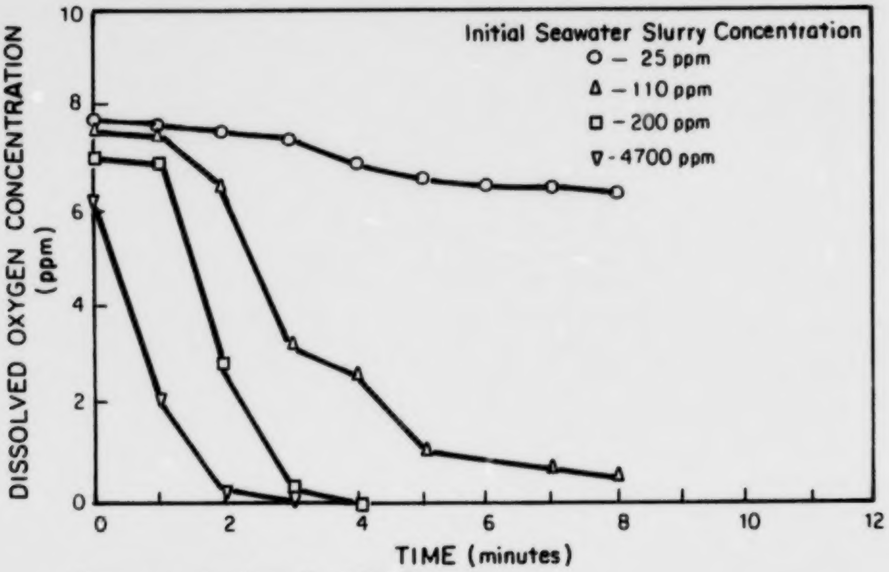
The effects of dissolution rate on oxygen depletion are further evidenced by the low rates of oxygen consumption measured in tests designed to simulate concentrated disposal by bottom-dump barge. Oxygen concentrations in the turbulent water column through which the wastes passed changed very little (<0.5 ppm). However, immediately above the impact area, there was a steady decrease in oxygen concentration with time, as shown in Figure IV-9.

c. Environmental Effects

Two principal concerns related to the sulfite fractions of certain FGC wastes were raised in the initial assessment. These were (1) the potential for direct toxicity to finfish of the available sulfite and (2) the potential for oxidation of the sulfite fraction to deplete the available dissolved oxygen in the disposal area. Work performed as part of this assessment has generally tended to reaffirm the concerns expressed in the initial assessment and to narrow the focus to the questions of oxygen depletion rather than sulfite toxicity.

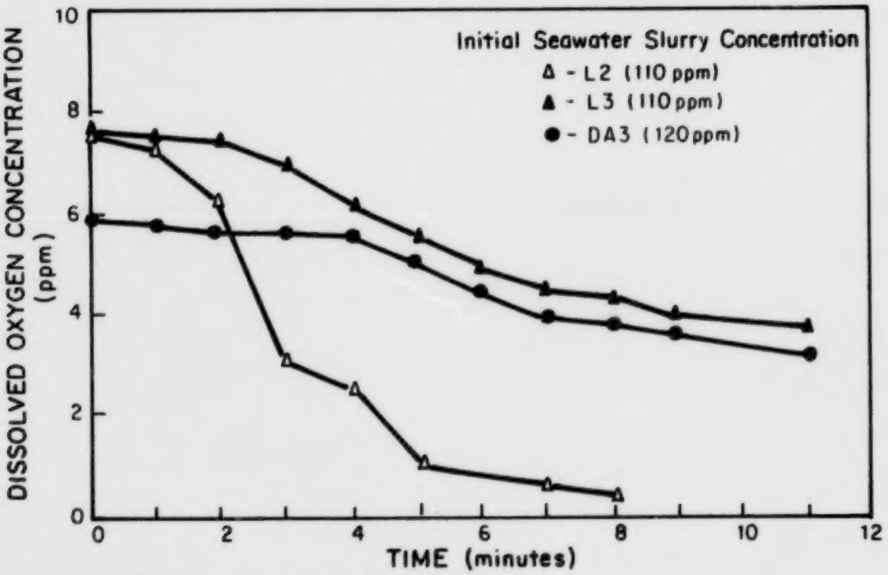
The dissolution tests conducted at Arthur D. Little, Inc. indicated that the highest sulfite concentration that may be encountered in seawater due to dissolution of FGC waste material is in the (1.6-2.4) x 10^{-3} M range. This is comparable to the median 50% lethal concentration for fish at pH 6 (0.001 M) observed under laboratory conditions (1). However, the more important results of the test series appear to be those which show rapid depletion of available dissolved oxygen by sulfite-rich waste (see Appendix B). In fact, it appears that oxygen depletion would be of far greater significance in the immediate vicinity of masses of sulfite-rich FGC waste in the ocean environment than would sulfite toxicity. Acute toxicity experiments to be performed as a part of the continuing test program are being designed to further pinpoint this impact potential from a biological perspective. The principal question pending resolution is expected to be the extent to which the descending waste masses create oxygen depletion problems given their relatively brief residence times in the water column. At the laboratory scale there were indications that dissolved oxygen depletion in simulated descent situations was considerably less significant than in situations involving thorough mixing and dissolution (e.g., slurries).

The initial assessment identified several trace contaminants known to be present in high concentrations in previously evaluated samples of FGC waste rich in fly ash. In descending order of concern, the potentially problematic contaminants, all trace metals, were: mercury; zinc; selenium, and cadmium. Trace contaminant impacts were not studied empirically in this updated assessment. However, literature reviews and



Source: Arthur D. Little, Inc.

FIGURE IV-7 OXYGEN DEPLETION VERSUS SLURRY CONCENTRATION FOR DIRECT-LINE SCRUBBER WASTE



Source: Arthur D. Little, Inc.

FIGURE IV-8 COMPARATIVE OXYGEN DEPLETION RATES FOR DIFFERENT SCRUBBER WASTES IN WELL-AGITATED SLURRIES

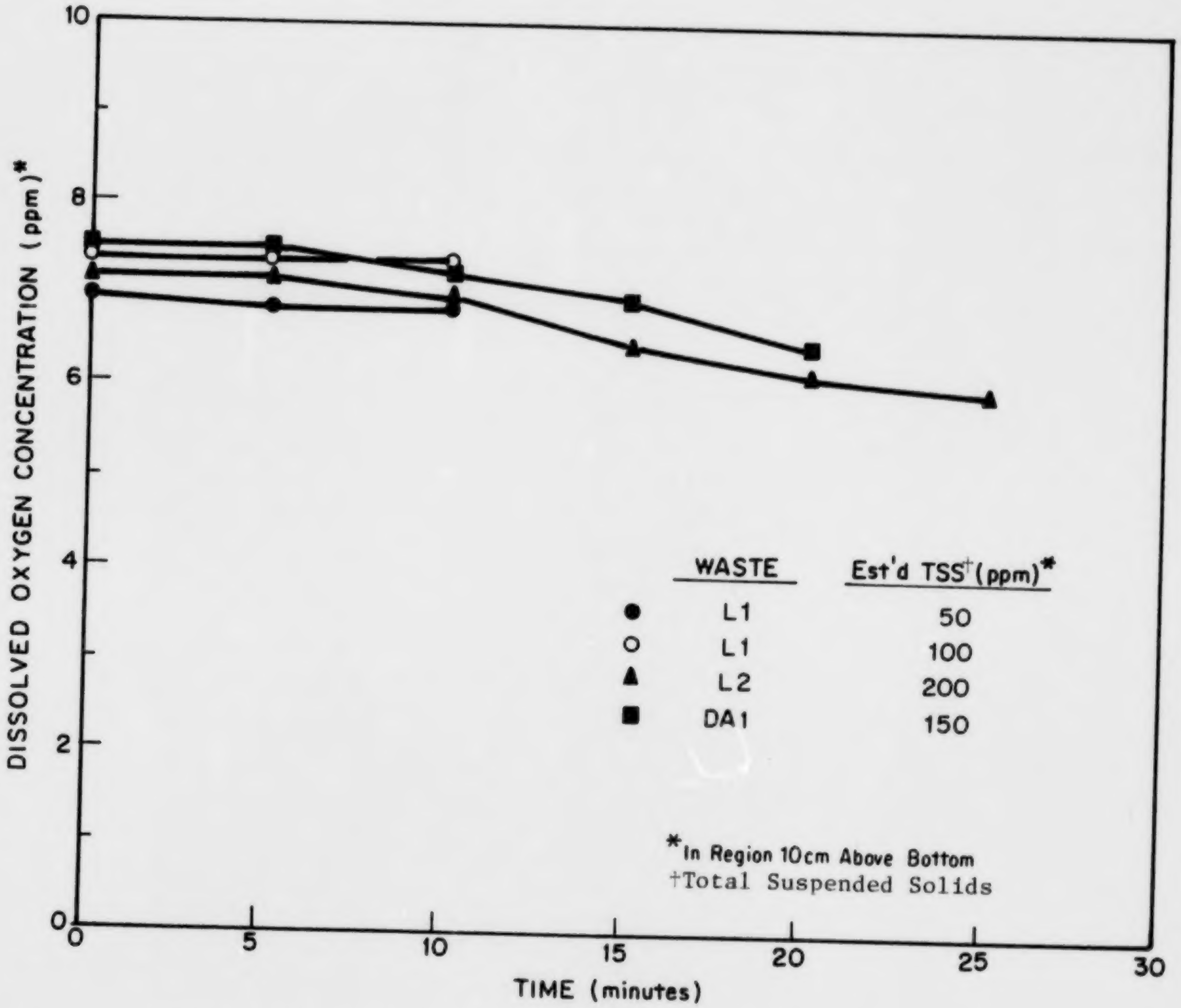


FIGURE IV-9 OXYGEN DEPLETION IN SMALL-SCALE DROP TESTS WITH FGC WASTES

Source: Arthur D. Little, Inc.

field interviews were continued, and the results of the dissolution/oxidation tests do give additional insight into trace contaminant impact potential. The dissolution test results confirm that, particularly for sulfate-rich wastes, rapid dissolution can be expected to contribute to the availability of much of the trace contaminant fractions for subsequent biological uptake. These considerations will be the focus of the upcoming tests of chronic toxicity and bioaccumulation.

C. REFINEMENT OF THE REGULATORY ASSESSMENT

1. Introduction

The statutory base for regulation of ocean dumping activities remained essentially unchanged since the initial assessment. The Marine Protection Research and Sanctuaries Act of 1972 (PL92-532) is still the basis for all domestic regulation of ocean dumping, and it has not been substantially amended since its passage. The inital assessment contains a summary discussion of its more important provisions. Major changes in the regulatory environment since the initial assessment have taken place in the form of amendments and revisions to the rules and regulations of the EPA concerning ocean dumping. The following discussion focuses on changes to the rules and regulations adopted with their publication in the January 11, 1977 Federal Register. In addition, a continuing series of contacts with key regulators in EPA's Office of Marine Protection, Office of General Counsel, and selected regional offices was conducted during the present work program, and the changes in attitudes and strategies reflected by those interviews are also discussed below.

2. Amendments to the Regulations and Criteria Governing Ocean Dumping

As was the case in the initial assessment, two sections of the ocean dumping regulations are particularly relevant to the subject of this report. These are sections 227 and 228, which respectively cover the criteria for the evaluation of permit applications for ocean dumping and the need for ocean dumping (227) and the criteria for the management of disposal sites for ocean dumping (228). Part 228 was added to the regulations since the time of the initial assessment, and major changes to part 227 took place during this same time frame. Changes in the following aspects of the regulations are discussed below:

- alternatives;
- prohibited materials;
- other factors limiting permissible concentrations;
- monitoring requirements;
- outfalls; and
- artificial reefs.

a. Consideration of Alternatives

At the time of the initial assessment it was anticipated that pending changes to the ocean dumping regulations would take place requiring the demonstration by dumping permit applicants that there was no feasible alternative to their proposed action. This consideration was adopted as part of the final ocean dumping regulations along with the other considerations spelled out in the initial assessment, with the modification that process alternatives need to be useful as well as technically feasible.

b. Prohibited Materials

Under the previous regulations, eastern FGC wastes could have been precluded from ocean disposal entirely on the basis of the cadmium content of the solid phase of many of the materials containing fly ash. This is because absolute limits existed on cadmium and mercury concentrations in both the solid and liquid phases of all materials. These limits were, for mercury, 1.5 ppm in the liquid phase of the waste and 0.75 ppm in the solid phase; and for cadmium, 3.0 ppm in the liquid phase and 0.6 ppm in the solid phase.

Mercury and cadmium are no longer listed as prohibited materials in the new regulations. This is perhaps the single most important change in the regulations with respect to FGC wastes. These substances are now listed as constituents prohibited as other than "trace contaminants," with a new set of interim and anticipated ultimate means of determining whether the "trace contaminant" definition applies. The current criterion for mercury in the liquid phase of the wastes to be dumped in the ocean is as follows:

> "...mercury concentrations in the disposal site, after allowance for initial mixing, may exceed the average normal ambient concentrations of mercury in ocean waters at or near the dumping site which would be present in the absence of dumping, by not more than 50%..."

A complementary criteria to be applied to all wastes including FGC wastes is a series of bioassay tests. The object of these tests is the identification of both acute and chronic toxicological impact potentials of the waste and the potential for bioaccumulation of toxicants in marine organisms as the result of exposure to the waste. The regulations indicated that bioassay procedures for suspended particulate and solid phases of waste materials were not sufficiently well developed to mandate the use of such tests as a prerequisite for permit approval. Thus, in the interim, while such procedures were being developed, the EPA personnel responsible for the administration of ocean disposal programs (usually at the regional level) were given a number of options for application review. With respect to mercury and cadmium in the suspended particulate and solid phases of wastes, the interim guidance was as follows.

Mercury and its compounds may be present in the solid phase of a material in concentrations less than 0.75 mg/kg or less than 50% greater than the average total mercury content in natural sediments of similar characteristics at the disposal site. Cadmium and its compounds in solid phase may be present in concentrations less than 0.6 mg/kg or, as with mercury, less than 50% greater than the total cadmium content of the natural sediments of similar characteristics at the disposal site. While these solid phase concentration numerical limits are identical to those in the previous regulation, the wide range in "natural" sediment concentrations of mercury and cadmium at disposal sites would ensure considerably greater flexibility than the previous regulations.

c. Other Factors Limiting Permissible Concentrations

In the previous regulation, absolute limits on the definition of a "mixing zone" existed. As noted in the initial assessment, proposed revisions to the regulations defined a "release zone" of 100-meter locus from the dumping conveyance during the dumping action but allowed for several means of defining the mixing zone. The revisions adding flexibility to mixing zone definitions through the use of evaluation techniques based on field data and predictive models were adopted essentially as described in the initial assessment.

The current regulations require that EPA's marine water quality criteria for various waste constituents to be met in the mixing zone four hours after the completion of dumping with the exception of the permissible 50% above-ambient increase for mercury noted above. The water quality criterion for cadmium was revised from .002 ppm to .005 ppm since the initial assessment. Assuming the same 500-fold dilution considered reasonable in the initial assessment, the resultant concentrations of cadmium in the mixing zone would be in the range of the original criterion and would, therefore, meet the revised criterion. However, there is still sufficient uncertainty as to the likelihood of such dilution to regard this calculation as little more than an indicator in the absence of bioassay (bioaccumulation tests) results.

d. Monitoring Requirements

The revised regulations contain a section 228 devoted to disposal site management including monitoring requirements and requirements for the evaluation of the environmental impacts of disposal activity. A major change in agency philosophy was reflected in these requirements. Previously, it appeared that permit applicants might be responsible for baseline and trend assessment monitoring at disposal sites. However, part 228 clearly spells out that these responsibilities belong to the Federal Government. Applicants' responsibilities are now confined to special monitoring programs designed case-by-case to determine short-term impacts of disposal activities.

Another important part of the revised regulation was the establishment of criteria for the evaluation of disposal impacts. In summary, these criteria establish a category of impacts (Category I) which, if identified at a disposal site, requires the EPA management authority to place limitations on use of the site to reduce impacts to acceptable levels. These Category I impacts include:

- statistically significant decrease in populations of valuable commercial or recreational species or species essential to the propagation of valuable commercial or recreational species;
- significant impairment of major uses of the site or adjacent areas due to accumulations of solid waste material;
- adverse effects on taste or odor of valuable commercial or recreational species as a result of disposal activities; or
- identification on a consistent basis of toxic concentrations of any toxic waste, waste constituent, or byproduct at levels above normal ambient values outside the disposal site more than four hours after disposal.

e. Regulation of Outfalls

In the initial assessment the regulation of outfalls was identified as an area of some ambiguity, and one that was in a state of flux. The revised regulations reflect some clarification of the outfall situation. Specifically, the newer regulations reflect the removal of ocean outfall discharges from the jurisdiction of the ocean dumping program. The outfalls are now subject to regulations pursuant to the authorities governing other outfalls under the Federal Water Pollution Control Act Amendments of 1972 (PL92-500). During the interviews conducted as part of this refined assessment, the outfall regulations appeared to be taking shape in a form somewhat related to the ocean dumping regulations but with a greater degree of flexibility and technology orientation. Specifically, while including consideration of acute bioassay testing results and the published marine water quality criteria, the then pending outfall regulations did not include extensive mandatory consideration of chronic bioassay or bioaccumulation tests, or specific focus on priority pollutants.

f. Artificial Reefs

The revised ocean dumping regulations (Section 220.1) specifically exempt from the ocean dumping permit requirements any structures or materials placed for the purpose of developing, maintaining, or harvesting fisheries resources, provided such placement or deposit is regulated under or is part of an authorized state or federal program with enforcement powers and that the National Oceanic and Atmospheric Administration (NOAA), the Coast Guard, and the Corps of Engineers concur with the placement of the artificial structure. This exemption could prove important in consideration of the disposal of certain classes of FGC wastes. In particular, treated brick-like FGC materials might qualify under certain disposal conditions as structures subject to the aforementioned exemption.

3. Agency Attitudes and Strategies

There appeared to be little basic change in the attitudes and strategies of personnel responsible for the administration of the ocean dumping regulations between the time of the initial and this refined assessment. However, a number of changes were noted and are discussed below.

During the interviews conducted as part of the initial assessment, many regulatory personnel at the regional level expressed their belief that ocean dumping was an activity to be phased out as well as strictly regulated. Other individuals including those responsible for policy making at the headquarters level indicated emphasis on strict regulation rather than phase-out. During the interviews conducted as part of this assessment a more uniform response was noted. In general, there seems to be consensus that the successes achieved by the agency and former dumpers in finding alternatives to ocean dumping make phase-out a realistic target in many, if not most, cases. Those responsible for the regulation of ocean dumping in Region VI (the Gulf Coast) exhibited a somewhat different approach. Those interviewed expressed a regulatory strategy focused on consideration of the economic/environmental tradeoffs involved in each permit application with consideration of rather than extensive emphasis on alternatives.

The second, perhaps greater change in attitude expressed during this assessment concerns the choices to be made between deep ocean and on-shelf dumping. In the initial assessment the prevailing attitude seemed to be that too little was known of the deep ocean environment to risk damages through disposal in the absence of elaborate and expensive monitoring programs. In the preparation of this assessment the prevalent attitude seemed to be that deep ocean disposal had some apparent ecological advantages and should not be discouraged through extensive (and likely futile) monitoring efforts at the expense of applicants. In fact, it appeared that in the East Coast regions where the most dumping has taken place and is likely to take place (Regions II and III), any new dumping would be required to use the "106 site" in 600-plus fathoms on the edge of the continental slope. The new regulations also reflect this revised attitude by allowing for certain less extensive monitoring requirements in waters greater than 200 fathoms in depth.

D. CONCLUSIONS AND RECOMMENDATIONS

1. Technical/Environmental Considerations

The two overall conclusions of the initial assessment are still considered valid. These conclusions pointed out the need for case-by-case analysis of disposal and affirmed the technical feasibility of available control options. Other specific initial conclusions have been reinforced by this assessment with some modifications as indicated below.

- Unless further work contradicts observed and anticipated benthic sedimentation impacts including mud flows, the disposal of untreated or treated FGC wastes with soil-like physical properties by bottom-dump barge or outfall on the continental shelf should be considered environmentally undesirable. As noted below, research relating to this option should be continued.

- The problems of disposal of sulfite-rich FGC wastes, both on and off the continental shelf, appear to be much greater than those associated with other FGC materials. There appear to be special grounds for concern over the potential for oxygen depletion in the vicinity of sulfite-rich waste masses. However, sulfite toxicity may be a relatively minor problem because of the significant rate of the oxidation reaction.

- Disposal options which still appear promising and are recommended for further research include:

  - dispersed disposal of untreated sulfate-rich FGC waste on the continental shelf;

  - concentrated disposal of treated brick-like FGC waste on the continental shelf;

  - dispersed disposal of treated brick-like FGC waste on the continental shelf;

  - dispersed disposal of untreated sulfate-rich FGC wastes in the deep ocean; and

  - concentrated disposal of all forms of sulfate-rich FGC wastes in the deep ocean.

2. Need for Additional Research and Information

The following research needs were believed most important at the conclusion of this assessment:

- Empirical bioassay data on the acute and/or chronic effects of sulfite-rich FGC wastes on representative marine organisms;
- Empirical bioassay data on the long-term availability and accumulation of FGC waste-related metallic trace contaminants;
- Empirical bioassay data on the suitability of soil-like FGC materials as benthic substrates in quiescent waters;
- The development of empirical data and verified theoretical models to predict field-scale FGC waste behavior during descent through marine water columns; and
- Continual investigation of field situations where FGC wastes have entered marine environments.

CHAPTER IV REFERENCES

1. Lunt, R.R., C.B. Cooper, S.L. Johnson, J.E. Oberholtzer, G.R. Schimke, and W.I. Watson, 1977. "An Evaluation of the Disposal of Flue Gas Desulfurization Wastes in Mines and the Ocean: Initial Assessment," EPA 600/7-77-051, U.S. Environmental Protection Agency, Office of Research and Development.

2. Mehta, A., 1973. "Depositional Behavior of Cohesive Sediments," Ph.D. thesis presented to the University of Florida.

3. Johnston, P.H., 1978. "The Effect of Fly Ash Addition on the Geotechnical Properties of FGD Sludges," M.Eng. thesis, University of Louisville, Louisville, Kentucky.

4. Hagerty, D.J., et al., June 1977. "Engineering Properties of FGD Sludges," Proceedings, Special Conference on Geotechnical Practices for Disposal of Solid Waste Materials, ASCE, Ann Arbor, Michigan. pp. 23-40.

5. Terzaghi, K. and R.B. Peck, 1967. Soil Mechanics in Engineering Practice, 2nd edition. John Wiley & Sons, New York.

6. Reed, A.W., 1975. Ocean Waste Disposal Practices, Noyes Data Corporation, Park Ridge, New Jersey.

7. Koh, R.C.Y. and Y.C. Chang, 1973. Mathematical Model for Barged Ocean Disposal of Wastes, Environmental Protection Technology Series, U.S. Environmental Protection Agency, Washington, D.C., EPA 660/2-73-029. 575 pp.

8. ERTS-1 satellite image of the New York Bight, August 16, 1972, as found in Stanley and Swift, Marine Sediment Transport and Environmental Management, 1976.

9. American Society of Civil Engineers, 1975. Sedimentation Engineering, manuals and reports on Engineering Practice No. 54. Vito A. Vanoni, editor. 750 pp.

10. Morton, J.W., 1976. "Ecological Impacts of Dredging and Dredge Spoil Disposal: A Literature Review," master's thesis presented to Cornell University, unpublished.

11. Masch, F.D. and W.H. Espey, Jr., 1967. "Shell dredging a factor in sedimentation at Galveston Bay," Center for Research in Water Resources, University of Texas, Austin, Texas. Technical Report HYD 06-6702, CRWR-7. 168 pp.

12. Bassi, D.E. and D.R. Basco, 1974. "Field study of an unconfined spoil disposal area of the Gulf Intercoastal Waterway in Galveston Bay, Texas." Texas A&M University, College Station, TX.TAMU-SG-74-208, C.O.E. Report No. 174. 74 pp.

13. U.S. Army Corps of Engineers, 1975. *Shore Protection Manual*, U.S. Army Coastal Engineering Research Center, Fort Belvoir, Virginia.

14. Madsen, O.S. and W.D. Grant, 1976. *Sediment Transport in the Coastal Environment*, Technical Report No. 209, MIT, Department of Civil Engineering, Ralph M. Parsons Laboratory, January 1976.

15. Personal communication, Prof. Ole S. Madsen, Massachusetts Institute of Technology. to Andrea Reyman, Arthur D. Little, Inc.

16. Hellier, T.R., Jr. and L.S. Kornicker, 1962. Sedimentation from a hydraulic dredge in a bay, Publ. Institute of Marine Science, University of Texas, 8:212-215.

17. Nittrouer, C.A. and R.W. Sternberg, 1975. "The fate of a fine-grained dredge spoils deposit in a tidal channel of Puget Sound, Washington," *Journal of Sediment. Petrol*., 45(1):160-170.

18. Saila, S.B., S.D. Pratt, and T.T. Polgar, 1972. *Dredge spoil disposal in Rhode Island Sound*, University of Rhode Island, Marine Technology Report No. 2.

19. Slotta, L.S., C.K. Sollitt, D.A. Bella, D.R. Hancock, J.E. McCauley, and R. Parr, 1973. *Effects of hopper dredging and in-channel spoiling in Coos Bay, Oregon*, Oregon State University, Corvallis, Oregon. 141 pp.

20. Smerdon, E.T. and R.P. Beasely, January 1961. "Critical Tractive Forces in Cohesive Soils," *Agricultural Engineering*, St. Joseph, Michigan. pp. 26-29.

21. Dunn, I.S., June 1959. "Tractive Resistance of Cohesive Channels," *Journal of the Soil Mechanics and Foundations Divisions*, ASCE, No. SM3, Proc. Paper 2062. pp. 1-24.

22. Partheniades, E., 1965. "Erosion and Deposition of Cohesive Soils," *Journal of the Hydraulics Division*, ASCE, Vol. 91, No. HYL, Proc. Paper 4204, pp. 105-139.

23. Flaxman, E.M., March 1963. "Channel Stability in Undisturbed Cohesive Soils," *Journal of the Hydraulics Division*, ASCE, Vol. 89, No. HY2, Proc. Paper 3462. pp. 87-96.

24. Pierce, J.W., 1976. "Suspended Sediment Transport at the Shell Break and Over the Outer Margin," *Marine Sediment Transport and Environmental Management*, Stanley and Swift, editors. John Wiley and Sons.

V. ECONOMIC CONSIDERATIONS FOR MINE DISPOSAL

A. BACKGROUND

The Initial Assessment of the disposal of FGC wastes in mines identified a number of possible options for waste handling, transportation and in-mine disposal (1). A number of questions and unresolved issues relating to the technical and engineering feasibility of such waste disposal operations were identified as needing additional throught and work. These questions and issues are further explored in Section III of this Refined Assessment.

In the Initial Assessment, some preliminary cost estimates were developed for a limited number of disposal scenarios covering both surface and underground mines. The purpose of the Refined Assessment is to develop more specific cost estimates for a set of waste disposal scenarios which are identified as promising options.

B. ENGINEERING COST ESTIMATES FOR DISPOSAL OPTIONS

The following disposal scenarios were developed to cover potential combinations of waste type, transportation mode and in-mine placement.

Six cases were considered:

Case E-1.	Lime scrubbing with stabilization, onsite mine disposal, Eastern coal.
Case E-2.	Limestone scrubbing with flyash, utilizing forced oxidation, onsite mine disposal, Eastern coal.
Case E-3.	Lime scrubbing with stabilization, offsite mine disposal, Eastern coal.
Case E-4.	Limestone scrubbing with fly ash, utilizing forced oxidation, offsite mine disposal, Eastern coal.
Case W-1.	Limestone scrubbing with fly ash, onsite mine disposal, Western coal.
Case W-2.	Limestone scrubbing with fly ash, offsite mine disposal, Western coal.

Capital costs and annual operating costs are presented for pit bottom disposal in each case, starting at the battery limits of the pug mill discharge belt. Consequently, these costs presented herein are exclusive of any costs associated with the handling and/or processing (thickening, filtration, etc.) operations which are required prior to the actual truck or rail transport of the waste to its ultimate disposal place, the mine. Rather, these capital and operating costs cover only the loading, transport, unloading and placement of the waste in the mine. However, the capital costs for all six cases under investigation do include costs for a stack-out area with radial stack-out conveyors. For cases E-1 and E-3 the stack-out area is required for waste curing, while for cases E-2, E-4, W-1 and W-2 the stack-out area is included as an emergency storage area in the case of the trucks or trains not being available for loading. Add-on capital costs and add-on operating costs were also estimated separately for V-Notch disposal and for compaction. Costs were expressed in mid-1980 dollars on the basis of instantaneous project investment costs.

Table V-1 presents the conceptual design basis used for the 1,000 MW power plant. Two boilers operate at a 70% annual load factor. The average operating heat rate was taken at 500 Btu/KWH more than the design heat rate of 9,500 Btu/KWH for Eastern coal and 10,000 Btu/KWH for Western coal. Compared to design conditions, the average operating conditions assumed a greater Higher Heating Value (HHV) and a lower sulfur and ash content for both Eastern and Western coals.

In the case of Western coals, average operating conditions assumed a smaller percentage of SO_2 removal, due to the assumption of low sulfur content. These operating parameters were used to develop the waste disposal system conditions that follow.

In Table V-2 the waste disposal system characteristics are described and waste flow calculations presented. For Eastern coal, particulate removal was accomplished by electrostatic precipitators. Two types of SO_2 removal were considered: conventional lime scrubbing which utilizes 85% CaO in 1.05 x stoichiometric ratio of CaO to SO_2, and provides a mixed waste stream of filtered FGD waste, dry fly ash and lime; and limestone scrubbing with forced oxidation, which utilizes 90% $CaCo_3$ in 1.2 x stoichiometric ratio of $CaCO_3$ to SO_2, and produces a mixed waste stream of filtered FGD waste and dry fly ash. For Western coal, particulate removal was accomplished by fabric filters and SO_2 removal by conventional limestone scrubbing, which utilizes 90% $CaCO_3$ in 1.1 x stoichiometric $CaCO_3$ to SO_2, and produces a mixed waste stream of thickened FGD and dry fly ash. Waste flows for design conditions were calculated in Tons Per Day (TPD); waste flows for average operating conditions were calculated in Thousands of Tons Per Year (1,000's TPY), and form the basis of estimating equipment and operational requirements for waste disposal transport and placement.

TABLE V-1

WASTE DISPOSAL CONCEPTUAL DESIGN BASES

SURFACE MINE DISPOSAL

	Eastern	Western
Boiler:		
Number Units	2	2
Net MW Each	500	500
Annual Load Factor	70%	70%
Btu/KWH - Design	9,500	10,000
- Average	10,000	10,500
Coal:		
Design - HHV (Btu/lb)	11,000	8,000
- Sulfur (%)	4.0	1.5
- Chloride (%)	0.2	0.05
- Ash (%)	16.0	20.0
Average- HHV (Btu/lb)	12,000	9,000
- Sulfur (%)	3.2	0.8
- Chloride (%)	0.05	0.02
- Ash (%)	12.0	15.0
Emissions Control:		
Design - SO_2 Removal (%)	90	85
- Particulate (%)	99+	99+
Average- SO_2 Removal (%)	90	70
- Particulate (%)	99+	99+

Source: Arthur D. Little, Inc.

TABLE V-2

WASTE DISPOSAL SYSTEM DESIGN CONDITIONS

SURFACE MINE DISPOSAL

	EASTERN		WESTERN
Control Technology			
SO_2	Conventional Lime	Limestone Forced Oxidation	Conventional Limestone
Particulate	Electrostatic Precipitator	Electrostatic Precipitator	Fabric Filter
Waste Processing	Filtered FGD[a] + Dry Flyash + Lime	Filtered FGD[b] + Dry Flyash	Thickened FGD[c] + Dry Flyash
Waste Flows:			
Design - Quantity (Tons Per Day)			
Dry FGD	1440[a]	1855[b]	590[c]
Dry Flyash	1315	1315	2380
Dry Waste	2755	3170	2970
Water	1550	650	1045
Subtotal Waste	4305	3820	4015
Dry Lime	120		
Total Waste	4425		
% Solids	65%	83%	74%
Operating - Quantity (1,000's Tons Per Year)			
Dry FGD	355	455	115
Dry Flyash	240	240	425
Dry Waste	595	695	540
Water	340	145	180
Subtotal Waste	935	840	720
Dry Lime	40		
Total Waste	975		
% Solids	65%	83%	75%

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[a] 85% CaO, 1.05 Stoichiometry on CaO
[b] 90% $CaCO_3$, 1.2 Stoichiometry on $CaCO_3$
[c] 90% $CaCO_3$, 1.1 Stoichiometry on $CaCO_3$

Source: Arthur D. Little, Inc.

Table V-3 describes the onsite and offsite equipment and operating characteristics for both Eastern and Western plants. Onsite mine disposal assumes a 4-mile (one way) truck haul of waste from the stackout area to the mine. Offsite mine disposal assumes a 100-mile (one way) rail haul of waste from the plant to the mine for Eastern plants and a 200-mile (one way) rail haul for Western plants.* Eastern plants require a 3-day cure period for the lime scrubbing waste, while no cure is required for limestone scrubbing. Both Eastern and Western plants utilize 35-ton trucks for onsite waste transport and 100-ton rail cars for offsite waste transport. Truck and train cycle times, loading operations and mine placement operations are specified in Table V-3. This information provides the basis for estimating capital and operating costs for each of the six cases presented below.

Case E-1. Lime scrubbing with stabilization, onsite mine disposal, Eastern coal.

Mixed, stablilized waste leaving the pub mills is stacked-out in a cure area for a 3-day cure period. The two-acre stack-out area is sized for 4 days of storage at annual average storage conditions. Stack-out is accomplished with a 200-ft long horizontal belt conveyor and an 80-ft tripping conveyor with a capacity of 200 Tons Per Hour (TPH), which stacks the waste in a linear orientation. Sludge is loaded by three front-end loaders (6 cubic yard capacity each) onto 35-ton capacity trucks on a two-shift basis, with the loaders operating about six hours out of every shift. The trucks taken about 30 minutes to load and about 45 minutes to make a round trip to the mine, including unloading at the mine. Eight trucks are required for this operation, of which six operate simultaneously, on the average. Additional capital requirements include the concrete stack-out pad with drain sump, runoff pumps and piping, a pickup truck, and 20 monitoring wells. For pit bottom disposal the trucks dump directly into the mine. If V-Notch disposal is used at the mine, one D-8 Dozer is required. If compaction is practiced at the mine, two additional D-8 Tractor Dozers are required. Table V-4 presents the capital costs for this case, and Table V-5 the operating costs and total costs per ton of waste.

Case E-2. Limestone scrubbing utilizing forced oxidation fly ash-blend, onsite mine disposal, Eastern coal.

Mixed waste leaving the pug mills is discharged directly into 35-ton rear dump trucks positioned at either end of a 60-ft horizontal reversing conveyor. An emergency, 100-ft radial stackout conveyor and a 1/2 acre concrete stackout area are provided in case trucks are not available. The trucks take 10 to 15 minutes to load and about 35 minutes to make a round trip to the mine, including unloading at the mine. Five trucks are required for this operation of which four operate simultaneously, on the average. Additional capital requirements include the concrete stackout pad with drain sump, runoff pumps and piping, one 5 cubic yard front-end loader, one pickup truck, and 20 monitoring wells. Add-ons for V-Notch disposal and for compaction are similar to Case E-1. Tables V-6 and V-7 present capital and operating costs for this case.

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*It is recognized that there would be many intermediate cases where an offsite mine is much closer to the plant (i.e., <20 miles). The 100-mile and 200-mile distances can be considered "outer boundary" assumptions for illustrative purposes.

TABLE V-3

WASTE DISPOSAL TRANSPORT/PLACEMENT OPTIONS

SURFACE MINE DISPOSAL

	ONSITE		OFFSITE	
Eastern	Lime	Limestone	Lime	Limestone
Distance (one way)	$\sim$ 4 Miles		100 Miles	
Transport	Truck		Rail	
Pre-cure Time	3-Day	None	3-Day	None
Loading	Front-end Loader	Direct & Front-end Loader	Dozer/Loader	
Vehicle Load Capacity	35-Ton		100-Ton	
Cycle Time	45 Minutes/Truck	35 Minutes/Truck	1 Train (30 Cars)/Day	
Loading Operation	2 Shifts/Day (7 Days)		1 Shift/Day (7 Days)	
Placement Operation	2 Shifts/Day (7 Days)		2 Shifts/Day (7 Days)	
Western	Limestone		Limestone	
Distance (one way)	$\sim$4 Miles		200 Miles	
Transport	Truck		Rail	
Pre-cure Time	None		None	
Loading	Direct & Front-end Loader		Dozer/Loader	
Vehicle Load Capacity	35-Ton		100-Ton	
Cycle Time	30 Minutes/Truck		3 Trains (60 Cars)/Week	
Loading Operation	2 Shifts/Day (7 Days)		1 Shift/Day (7 Days)	
Placement Operation	2 Shifts/Day (7 Days)		2 Shifts/Day (7 Days)	

Source: Arthur D. Little, Inc.

TABLE V-4

CAPITAL COST ESTIMATE, CASE E-1

EASTERN SURFACE MINE (ONSITE)

LIME SCRUBBING WITH STABILIZATION [a]

DISPOSAL MODE	EQUIPMENT	DESCRIPTION	NO.	TOTAL COST
Pit Bottom/Direct Dump				
	Installed Equipment			
	Stacker Conveyor	200 foot Horizontal Belt w/ Tripper-200 TPH†	1	$335,000
	Stacker Area	2-Acre Concrete Pad w/Drain Sump	1	280,000
	Runoff Pumps & Piping		2	95,000
	SUBTOTAL			$710,000
	Mobile Equipment			
	Haul Trucks	35-ton, Rear Dump	8	$1,480,000
	Loaders	6 cubic yard (360 Horsepower)	3	630,000
	Pickup Truck		1	20,000
	SUBTOTAL			$2,130,000
	Monitoring (Install/Secure/Establish Wells)		20 wells*	280,000
	TOTAL			$3,120,000
Add On For V-Notch Disposal				
	Dozers	D-8 (for access)	1	$ 180,000
Add On For Compaction				
	Dozers	D-8 Tractor	2	$ 360,000

*Includes geohydrology survey and permitting.

†Tons Per Hour

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[a] These costs do not include any costs associated with the handling and/or processing (thickening, filtration, etc.) operations which are required prior to the actual truck or rail transport of the waste to the mine for ultimate disposal. These costs cover only the loading, transport, unloading and placement of the waste in the mine.

Source: Arthur D. Little, Inc.

TABLE V-5

OPERATING COST ESTIMATE, CASE E-1
EASTERN SURFACE MINE (ONSITE)
LIME SCRUBBING WITH STABILIZATION[a]

ITEM	UNITS	$/UNIT	UNITS/YEAR	$1,000/YEAR*
Pit Bottom/Direct Dump				
Labor				
Oper. Labor	Man-Hours	$15.00	52,560	$ 790
Supervision	Man-Years	25,000	2	50
Power	Kilowatt Hours	.04	435,000	20
Fuel (Diesel)	Gallons	.80	650,000	520
Maintenance				
Installed Equip.	@6% of Capital Cost			40
Mobile Equip.	Op. Hrs.(Nominal)	12.00	46,720	560
Monitoring				
Labor/Permitting	Man-Hours	16.00	3,000	50
Analyses	--	--	--	40
Overhead/Administration	(30% of total operating labor)**			375
Capital Charges				
10-year Replacement of Mobile Equipment				210
18% on Installed Equipment				130
	TOTAL			$2,785
	$/wet ton total (dry ton)		$2.86 ($4.38)	
Add-on for V-Notch Disposal			$0.29 ($0.44)	280
Add-on for Compaction			$0.57 ($0.88)	560

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[a] These costs do not include any costs associated with the handling and/or processing (thickening, filtration, etc.) operations which are required prior to the actual truck or rail transport of the waste to the mine for ultimate disposal. These costs cover only the loading, transport, unloading and placement of the waste in the mine.

*Rounded off to nearest $5,000.

**Labor costs include operating labor ($790,000), supervision ($50,000), 50% of the cost of installed equipment maintenance ($20,000), 60% of the cost of mobile equipment maintenance ($280,000), and monitoring labor, adding up to $1,245,000, of which 30% is $375,000.

Source: Arthur D. Little, Inc.

TABLE V-6

CAPITAL COST ESTIMATE, CASE E-2
EASTERN SURFACE MINE (ONSITE)
LIMESTONE SCRUBBING/FLYASH BLENDED[a]

DISPOSAL MODE	EQUIPMENT	DESCRIPTION	NO.	TOTAL COST
Pit-Bottom/Direct Dump				
	Installed Equipment			
	Reversing Conveyor & Chutes	60 Foot Horizontal	1	$125,000
	Stacking Conveyor	100 Foot Radial	1	140,000
	Stackout Area	1/2 Acre (Concrete)		90,000
	Runoff Pumps & Piping		2	70,000
	SUBTOTAL			$425,000
	Mobile Equipment			
	Haul Trucks	35-Ton, Rear Dump	5	$925,000
	Loaders	5-Cubic Yard (325 HP)	1	185,000
	Pickup Truck		1	20,000
				$1,130,000
	Monitoring			280,000
	TOTAL			$1,835,000
Add-On for V-Notch Disposal				
	Dozers	D-8	1	$180,000
Add-On for Compaction				
	Dozers	D-8	2	$360,000

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[a] These costs do not include any costs associated with the handling and/or processing (thickening, filtration, etc.) operations which are required prior to the actual truck or rail transport of the waste to the mine for ultimate disposal. These costs cover only the loading, transport, unloading and placement of the waste in the mine.

Source: Arthur D. Little, Inc.

TABLE V-7

OPERATING COST ESTIMATE, CASE E-2
EASTERN SURFACE MINE (ONSITE)
LIMESTONE SCRUBBING/FLYASH BLENDING [a]

ITEM	UNITS	$/UNIT	UNITS/YEAR	$1,000/YEAR*
Pit Bottom/Direct Dump				
Labor				
Operating Labor	Man-Hours	$15.00	32,120	$ 480
Supervision	Man-Years	25,000	2	50
Power	Kilowatt Hour	.04	220,000	10
Fuel	Gallons	.80	600,000	480
Maintenance				
Installed Equipment	@6% of Capital Cost			25
Mobile Equip.	Op. Hrs. (Nominal)	12.00	29,200	350
Monitoring				
Labor/Permitting	Man-Hours	16.00	3,000	50
Analyses				40
Overhead/Administration (30% of total operating labor)**				240
Capital Charges				
10-year Replacement of Mobile Equipment				115
18% of Installed Equipment				75
TOTAL				$1,915
$/wet ton total (dry ton)			$2.26 ($2.74)	
Add-on V-Notch Disposal			$0.33 ($0.40	280
Add-on for Compaction			$0.66 ($0.80)	560

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[a] These costs do not include any costs associated with the handling and/or processing (thickening, filtration, etc.) operations which are required prior to the actual truck or rail transport of the waste to the mine for ultimate disposal. These costs cover only the loading, transport, unloading and placement of the waste in the mine.

*Rounded off to nearest $5,000.

**See footnote, Table V-5.

Source: Arthur D. Little, Inc.

Case E-3. Lime scrubbing with stabilization, offsite mine disposal, Eastern coal.

Mixed, stabilized waste leaving the pug mills is stacked out in a cure area for a 3-day cure period. The three-acre stack-out area is sized for 6 days of storage at annual average storage conditions. Stack-out is accomplished with two, 150-foot long radial stacker belt conveyors operating off of one 100-foot long horizontal reversing conveyor to provide full cure area coverage. Waste is loaded into rail cars which are below grade by two wheeled Dozers which feed into chute hoppers located above the load station. Loading takes 10 to 15 minutes per car, and about 30 cars per day are loaded on a one-shift per day, 7-day per week basis. The rail cars are 100-ton capacity, bottom dump coal cars. At the mine, the cars are rotary-dumped onto unloading conveyors which feed a stacking conveyor. Three, 6 cubic yard front-end loaders are used to load eight, 35-ton trucks for 2-mile haulage to the mine pit or V-Notch. Placement of waste at the mine is on a 2 shift per day, 7 day per week basis. Additional capital requirements at the power plant include concrete stack-out pad with drain sump, runoff pumps and piping, lowered track siding, two 5 cubic yard front-end loaders, pickup truck, and monitoring wells. At the mine, in addition to the conveyors, loaders and hauling trucks, there are rotary dumpers, track hoppers, a building and discharge area, pipe and pumps, and a pickup truck. Add-ons for V-Notch disposal and compaction are the same as for Case E-1. Tables V-8 and V-9 present capital and operating costs for this case.

Case E-4. Limestone scrubbing utilizing forced oxidation, fly ash-blend, offsite mine disposal, Eastern coal.

Mixed waste leaving the pug mills is stacked out in a 1-1/2 acre, concrete stackout area which is sized for three days of storage at annual average conditions if trains are not available. Stack-out is accomplished with a 200-foot horizontal tripper conveyor. Waste is loaded into rail cars which are below grade by two wheeled Dozers which feed into chute hoppers located above the load station. Loading takes 10 to 15 minutes per car, and about 30 cars per day are loaded on a one shift per day, 7 day per week basis. The rail cars are 100-ton capacity, bottom dump coal cars. Unloading at the mine is the same as for Case E-3, as are capital equipment requirements. Tables V-10 and V-11 present capital and operating costs for this case.

Case W-1. Conventional limestone scrubbing, fly ash-blend, onsite mine disposal, Western coal.

This case is the same as Case E-2-- same description, capital costs, and operating costs. However, since the annual tonnage of waste produced is less than for Case E-2, the per ton cost of waste disposal is higher:

$/wet ton total (dry ton)	$2.65	($3.55)
Add-on for V-Notch Disposal	$0.39	($0.52)
Add-on for Compaction	$0.77	($1.04)

TABLE V-8

CAPITAL COST ESTIMATE, CASE E-3
EASTERN SURFACE MINE (OFFSITE)
LIME SCRUBBING WITH STABILIZATION[a]

LOCATION	EQUIPMENT	DESCRIPTION	NO.	TOTAL COST
Power Plant				
Installed Equipment/Systems				
	Stacker Conveyors	150 Foot Radial	2	$380,000
	Reversing Conveyor	100 Foot Horizontal	1	150,000
	Stackout Area & Hoppers	3-Acres	-	840,000
	Lowered Track Siding		-	620,000
	Sump Pumps/Piping		2	130,000
	SUBTOTAL			$2,120,000
Mobile Equipment				
	Dozers	Wheeled	2	280,000
	Front-End Loaders	5-Cubic Yard	2	320,000
	Pickup Truck		1	20,000
	SUBTOTAL			620,000
	PLANT SUBTOTAL			$2,740,000
Mine Receiving/Placement				
Installed Equipment				
	Rotary Dumpers		2	$1,200,000
	Track Hoppers		2	60,000
	Pipe & Pumps		-	45,000
	Building & Discharge Area		1	340,000
	Unloading Conveyor		1	140,000
	Stacking Conveyor		1	180,000
	SUBTOTAL			$1,965,000

TABLE V-8

(continued)

LOCATION	EQUIPMENT	DESCRIPTION	NO.	TOTAL COST
Mine Receiving/Placement				
Mobile Equipment				
	Hauling Trucks	35-Ton	8	$1,480,000
	Loaders	6-Cubic Yard	3	630,000
	Pickup Truck		1	20,000
	SUBTOTAL			$2,130,000
Monitoring				280,000
	TOTAL			$7,115,000
Add-on for V-Notch Disposal				
	Dozers	D-8	1	180,000
Add-on for Compaction				
	Dozers	D-8	2	360,000

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[a] These costs do not include any costs associated with the handling and/or processing (thickening, filtration, etc.) operations which are required prior to the actual truck or rail transport of the waste to the mine for ultimate disposal. These costs cover only the loading, transport, unloading and placement of the waste in the mine.

Source: Arthur D. Little, Inc.

TABLE V-9

OPERATING COST ESTIMATE, CASE E-3

EASTERN SURFACE MINE (OFFSITE)

LIME SCRUBBING WITH STABILIZATION[a]

ITEM	UNITS	$/UNIT	UNITS/YEAR	$1,000/YEAR*
Pit Bottom/Direct Dump				
Labor				
Op. Labor	Man-Hours	$15.00	67,120	$1,005
Supervision	Man-Years	25,000	3	75
Power	Kilowatt Hours	0.04	620,000	25
Fuel (Diesel)	Gallons	0.80	490,000	390
Maintenance				
Installed Equip. @6% of Capital Cost				245
Mobile Equip.	Op. Hrs (Nominal)	12.00	58,400	700
Rail Haul Fee	Ton-mile	0.035	1.01×10^8	3,535
Monitoring				
Labor/Permitting	Man-Hours	16.00	4,000	65
Analyses				50
Overhead/Administration (40% of total operating labor)**				675
Capital Charges				
10-year Replacement of Mobile Equipment				275
18% of Installed Equipment				735
	TOTAL			$7,775
	$/wet ton total (dry ton)		$8.00 ($12.23)	
Add-on for V-Notch Disposal			$0.29 ($00.44)	280
Add-on for Compaction			$0.57 ($00.88)	560

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[a] These costs do not include any costs associated with the handling and/or processing (thickening, filtration, etc.) operations which are required prior to the actual truck or rail transport of the waste to the mine for ultimate disposal. These costs cover only the loading, transport, unloading and placement of the waste in the mine.

*Rounded off to nearest $5,000.

**See footnote, Table V-5.

Source: Arthur D. Little, Inc.

TABLE V-10

CAPITAL COST ESTIMATE, CASE E-4

EASTERN SURFACE MINE (OFFSITE)

LIMESTONE SCRUBBING/FLYASH BLENDING [a]

LOCATION	EQUIPMENT	DESCRIPTION	NO.	TOTAL COST
Power Plant				
Installed Equipment/Systems				
	Tripper Conveyer	200 Foot Horizontal	1	$335,000
	Stackout Area & Hopper	1-1/2 Acres		510,000
	Lowered Track Siding			620,000
	Sump Pumps/Piping		2	130,000
SUBTOTAL				$1,595,000
Mobile Equipment				
	Dozers Wheeled		2	280,000
	Front-End Loaders, 5-Cubic Yard		2	320,000
	Pickup Truck		1	20,000
SUBTOTAL				620,000
PLANT SUBTOTAL				$ 2,215,000
Mine Receiving/Placement				
Installed Equipment				
	Rotary Dumpers		2	$ 1,200,000
	Track Hoppers		2	60,000
	Pipe & Pumps		-	45,000
	Building & Discharge Area		1	340,000
	Unloading Conveyor		1	140,000
	Stacking Conveyor		1	180,000
SUBTOTAL				$1,965,000

TABLE V-10

(continued)

LOCATION	EQUIPMENT	DESCRIPTION	NO.	TOTAL COST
Mine Receiving/Placement				
Mobile Equipment				
Hauling Trucks		35-Ton	8	$1,480,000
Loaders		6-Cubic Yard	3	630,000
Pickup Truck			1	20,000
SUBTOTAL				$2,130,000
Monitoring				$ 280,000
TOTAL				$6,590,000
Add-On For V-Notch Disposal				
	Dozers	D-8	1	$ 180,000
Add-On For Compaction				
	Dozers	D-8	2	$ 360,000

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[a] These costs do not include any costs associated with the handling and/or processing (thickening, filtration, etc.) operations which are required prior to the actual truck or rail transport of the waste to the mine for ultimate disposal. These costs cover only the loading, transport, unloading and placement of the waste in the mine.

Source: Arthur D. Little, Inc.

TABLE V-11

OPERATING COST ESTIMATE, CASE E-4
EASTERN SURFACE MINE (OFFSITE)
LIMESTONE SCRUBBING/FLYASH BLENDING[a]

ITEM	UNITS	$/UNIT	UNITS/YEAR	$1,000/YEAR[*]
Pit-Bottom/Direct Dump				
Labor				
Operating Labor	Man-Hours	$ 15.00	61,320	$ 920
Supervision	Man-Years	25,000	3	75
Power	Kilowatt Hour	.04	580,000	25
Fuel (Diesel)	Gallons	0.8	460,000	370
Maintenance				
Installed Equipment @ 6% of Capital Cost				215
Mobile Equipment Operating Hours (Nominal)		12.00	58,400	700
Rail Haul Fee	Ton-Miles	0.035	0.92×10^8	3,220
Monitoring				
Labor/ Permitting	Man-Hours	16.00	4,000	65
Analyses				50
Overhead/Administration (40% of Total Operating Labor)**				635
Capital Charges				
10-year Replacement of Mobile Equipment				275
18% of Installed Equipment				640
	TOTAL			$7,190
	$/wet ton total (dry ton)		$8.50 ($10.98)	
Add-On for V-Notch Disposal		$0.33 ($0.40)		280
Add-On for Compaction		$0.66 ($0.80)		560

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[a] These costs do not include any costs associated with the handling and/or processing (thickening, filtration, etc.) operations which are required prior to the actual truck or rail transport of the waste to the mine for ultimate disposal. These costs cover only the loading, transport, unloading and placement of the waste in the mine.

[*] Rounded off to nearest $5,000.

[**] See footnote, Table V-5.

Source: Arthur D. Little, Inc.

Case W-2. Conventional limestone scrubbing, fly ash-blend, offsite mine disposal, Western coal.

This case is similar in description to Case E-3 except that there is no cure period for the waste, and train loading is done on a different schedule. Three trains of 60 cars each are loaded every week, and the loading of a single train takes about ten hours. The one way distance from the plant to the mine is assumed to be 200 miles. Stacking and unloading conveyors at the mine are about one-third larger than for Case E-3, and one less truck is required at the mine. Tables V-12 and V-13 present capital and operating costs for this case.

The per ton costs of waste disposal, wet and dry, are summarized for all six cases in Table V-14.

C. COMPARISON OF PROJECTED COSTS FOR MINE DISPOSAL WITH THOSE FOR OTHER DISPOSAL MODES

A number of conceptual design and cost studies have been undertaken sponsored by governmental agencies and private organizations, notably the EPA and EPRI. These studies have been basically of two types: (1) generalized costing to develop comparative economics for various waste disposal options, including current practices and potential alternatives; and (2) economic impact analyses to estimate the effects of various FGC waste disposal regulatory scenarios on the utility industry. Unfortunately, however, the design and operating assumptions in these economic studies as well as the battery limits for the disposal systems differ. Also, costs are generally presented in lump sum form covering both the waste processing and disposal facilities. Hence, direct comparisons of cost estimates are difficult at best.

In light of all this, the only type of comparison that can be made between the surface mine waste disposal costs reported herein and other type waste disposal costs is a very generalized one. For example, for the onsite mine disposal cases (Case E-1, E-2, and W-1) the cost for V-Notch mine disposal (excluding compaction) ranges from a low of $3.15/dry ton for blended FGD waste (forced oxidation) and western fly ash to a high of $4.85 for stabilized FGD waste; with an intermediate of $4.05/dry ton for blended FGD waste and western fly ash. The transport and placement costs for the onsite landfilling of similar type and quantity wastes in a managed fill would (within the accuracy of these estimates) roughly be in the same range to about 15-25% higher due to higher land and mobile equipment capital costs, and increased disposal labor and mobile equipment operating costs. Higher operating costs for a managed landfill are partly due to the fact that with a landfill there are reclamation costs while reclamation is a normal part of mine operations.

In contrast, for the offsite mine disposal cases (Case E-3, E-4, and W-2) the cost for V-Notch mine disposal (excluding compaction) ranges from a low of $10.70/dry ton for blended FGD waste (forced oxidation) and eastern fly ash to a high of $19.15/dry ton for blended FGD waste

TABLE V-12

CAPITAL COST ESTIMATE, CASE W-2
WESTERN SURFACE MINE (OFFSITE)
LIMESTONE SCRUBBING/FLYASH BLEND[a]

LOCATION	EQUIPMENT	DESCRIPTION	NO.	TOTAL COST
Power Plant				
Installed Equipment/Systems				
	Stacker Conveyors	150 Foot Radial	2	$380,000
	Reversing Conveyor	100 Foot Horizontal	1	150,000
	Stackout Area and Hoppers	3-Acres	-	840,000
	Lowered Track Siding		-	620,000
	Sump Pumps/Piping		2	130,000
	SUBTOTAL			$2,120,000
Mobile Equipment				
	Dozers	Wheeled	2	280,000
	Front-End Loaders	5-Cubic Yard	2	320,000
	Pickup Truck		1	20,000
	SUBTOTAL			620,000
	PLANT SUBTOTAL			$2,740,000
Mine Receiving/Placement				
Installed Equipment				
	Rotary Dumpers		2	$1,200,000
	Track Hoppers		2	60,000
	Pipe & Pumps		-	45,000
	Building & Discharge Area		1	340,000
	Unloading Conveyor		1	190,000
	Stacking Conveyor		1	240,000
	SUBTOTAL			$2,075,000

TABLE V-12

(continued)

LOCATION	EQUIPMENT	DESCRIPTION	NO.	TOTAL COST
Mine Receiving/Placement				
Mobile Equipment				
	Hauling Trucks	35-Ton	8	$1,295,000
	Loaders	6-Cubic Yard	3	630,000
	Pickup Truck		1	20,000
	SUBTOTAL			$1,945,000
Monitoring				280,000
	TOTAL			$7,040,000
Add-On For V-Notch Disposal				
	Dozers	D-8	1	$ 180,000
Add-On For Compaction				
	Dozers	D-8	2	$ 360,000

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[a] These costs do not include any costs associated with the handling and/or processing (thickening, filtration, etc.) operations which are required prior to the actual truck or rail transport of the waste to the mine for ultimate disposal. These costs cover only the loading, transport, unloading and placement of the waste in the mine.

Source: Arthur D. Little, Inc.

TABLE V-13

OPERATING COST ESTIMATE, CASE W-2
WESTERN SURFACE MINE (OFFSITE)
LIMESTONE SCRUBBING/FLYASH BLENDING[a]

ITEM	UNITS	$/UNIT	UNITS/YEAR	$1,000/YEAR*
Pit-Bottom/Direct Dump				
Labor				
Operating Labor	Man-Hours	$ 15.00	57,224	860
Supervision	Man-Years	25,000	3	75
Power	Kilowatt Hour	0.04	660,000	25
Fuel (Diesel)	Gallons	0.80	460,000	370
Maintenance				
Installed Equipment @ 6% of Capital Cost				
Mobile Equipment				
Operating Hours (Nominal)		12.00	55,480	665
Rail Haul Fee	Ton-Miles	0.035	1.74×10^8	6,090
Monitoring				
Labor/ Permitting	Man-Hours	16.00	4,000	65
Analyses				50
Overhead/Administration (40% of Total Operating Labor)**				610
Capital Charges				
10-year Replacement of Mobile Equipment				255
18% of Installed Equipment				755
TOTAL				$10,070
$/wet ton total (dry ton)			$13.93 ($18.65)	
Add-On for V-Notch Disposal		$0.39 ($0.52)		280
Add-On for Compaction		$0.77 ($1.04)		560

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[a] These costs do not include any costs associated with the handling and/or processing (thickening, filtration, etc.) operations which are required prior to the actual truck or rail transport of the waste to the mine for ultimate disposal. These costs cover only the loading transport, unloading and placement of the waste in the mine.

*Rounded off to nearest $5,000.

**See footnote, Table V-5.

Source: Arthur D. Little, Inc.

TABLE V-14

ESTIMATED PER TON COST OF FGC WASTE DISPOSAL IN SURFACE MINES 1,000 MW PLANT[a]

Case Number And Description	Units: $ per Ton Waste					
	Pit-Bottom		Add-On For V-Notch		Add-On For Compaction	
	Wet	Dry	Wet	Dry	Wet	Dry
E-1. Lime scrubbing with stabilization, onsite mine disposal, Eastern coal.	2.85	4.40	0.30	0.45	0.55	0.90
E-2. Limestone scrubbing with flyash, forced oxidation, onsite disposal, Eastern coal.	2.25	2.75	0.35	0.40	0.65	0.80
E-3. Lime scrubbing with stabilization, offsite mine disposal, Eastern coal.	8.00	12.25	0.30	0.45	0.55	0.90
E-4. Limestone scrubbing with flyash, forced oxidation, offsite disposal, Eastern coal.	8.50	10.30	0.35	0.40	0.65	0.80
W-1. Limestone scrubbing with flyash, onsite mine disposal, Western coal.	2.65	3.55	0.40	0.50	0.80	1.05
W-2. Limestone scrubbing with flyash, offsite mine disposal, Western coal.	13.95	18.65	0.40	0.50	0.80	1.05

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[a] These costs do not include any costs associated with the handling and/or processing (thickening, filtration, etc.) operations which are required prior to the actual truck or rail transport of the waste to the mine for ultimate disposal. These costs cover only the loading, transport, unloading and placement of the waste in the mine.

Source: Arthur D. Little, Inc.

(forced oxidation) and western fly ash; with an intermediate of \$12.70/dry ton for stabilized FGD waste. These offsite mine disposal costs are not only anywhere from 2-1/2 to 5 times greater than those costs for the onsite mine disposal of similar type and quantity of wastes, but would be about 2 to 4 times greater than offsite disposal in a managed landfill. However, one must remember that the offsite mine disposal costs herein are probably quite inflated by the assumption of 100-mile and 200-mile rail-haul distances.

It must be noted that the range of operating costs presented herein do not include the additional costs associated with the handling/processing (thickening, filtration, stabilization, etc.) operations which are required prior to the transportation and ultimate disposal of the particular waste. Consequently, if the additional cost elements for these operations are included, not only will the magnitude of all the disposal costs (\$/dry ton) presented increase considerably, but the relative difference between one type of disposal and another may also be affected.

APPENDIX A

MINE DISPOSAL LABORATORY STUDIES

In order to help in the evaluation of the feasibility of disposal of FGC wastes in mines, laboratory studies were conducted to generate data on:

a) Sulfite levels in groundwater due to leaching from the waste;

b) Sulfur dioxide evolution from reaction of sulfite-rich waste with acid mine drainage water;

c) Change in dewatering properties of the waste upon freeze/thawing.

The experiments performed in each of these areas are described below. Compositions of the suite of FGC waste samples are given in Table A-1.

A. GROUNDWATER LEACHING OF SULFITE FROM SULFITE-RICH SLUDGE

1. Description of Experiments

The leaching of sulfite from sulfite-rich waste by permeating groundwaters is expected to occur by two mechanisms. The first involves release of the remaining sulfite scrubber liquor in the waste by displacement as the groundwater passes through. In the absence of oxidation, the sulfite level in the released liquor would be expected to be identical to that of the original liquid present in the waste. The second mechanism of sulfite leaching involves dissolution of the calcium sulfite into the groundwater. Since permeation of groundwater through the waste is much slower than the dissolution rates (see ocean studies -- Appendix B), the exiting groundwater would be expected to be saturated with respect to calcium sulfite under anaerobic conditions.

The sulfite level present in the liquid phase of the waste material is dependent on the process from which the waste was produced. On the other hand, the equilibrium sulfite level in contact with the groundwater is expected to be more variable since the solubility of calcium sulfite depends on the chemical species present in the groundwater. Since the character of groundwater varies from place to place, the sulfite level could be predicted accurately if one had an understanding of the individual effects of each of the major constituents in groundwater. Such a study is beyond the scope of this work. An attempt was made, however, to investigate the effect of variations in concentration of some species which would be expected to have the largest effect on the solubility of $CaSO_3$. The factors which should be considered are those that can affect the activity of calcium and sulfite ions, such as: the total ion concentrations (ionic strength), the presence of complexing agents, such as Ca^{++} and Mg^{++} which can form complexes with sulfite, and the presence of $SO_4^{=}$ which can complex with calcium.

TABLE A-1

MAJOR CONSTITUENTS OF FGC WASTE SAMPLES FOR THIS PROGRAM

System	Sample Designation	Form	Type	Simultaneous Ash Removal	Wt % Solids[a]	Chemical Analysis (mmols/gm-dry) Ca	Mg	Na	TOS[b]	SO_4	Cl	Wt% Acid Insolubles	Use in Disposal Testing[f]
Dual Alkali	DA1	Filter Cake	Sulfite-Rich	No	54	7.15	0.25	0.43	5.60	0.97	0.04	0	O
	DA2[c]	Filter Cake	Sulfite-Rich	No	63	-	-	-	5.88	-	-	-	B
	DA3	Filter Cake	Sulfite-Rich	Yes	57	4.45	0.22	0.22	2.66	0.87	0.03	31	B
	DA4	Filter Cake	Sulfite-Rich	No	98[d]	7.41	0.14	0.21	5.11	1.28	0.02	3	--
Direct Lime	L1	Centrifuge Cake	Sulfite-Rich	Yes	63	4.59	0.05	0.03	3.85	0.70	0.05	35	B
	L2	Filter Cake	Sulfite-Rich	No	52	7.22	0.07	0.03	5.76	1.37	0.03	1	B
	L3	Filter Cake	Sulfite-Rich	No	47	6.99	0.23	0.02	5.89	0.52	0.01	3	O
Direct Limestone	LS1	Filter Cake	Sulfite-Rich	Yes	57	6.48	0.07	0.03	3.04	0.64	0.09	25	--
	LS2	Filter Cake	Sulfate-Rich	Yes	79	4.20	0.04	0.03	0.01	3.69	0.05	38	--
	LS3	Thickener Underflows	Sulfite-Rich	No	59[e]	7.06	0.07	0.03	5.24	0.99	0.05	6	M
ACS Scrubbing	G1	Centrifuge Cake	Sulfate-Rich	No	83	6.05	0.01	0.02	0.00	6.04	<0.01	< 1	O

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a) As received.
b) Total Oxidizable Sulfur ($HSO_3^- + SO_3^=$).
c) Insoluble in 1 molar HCl.

Source: Arthur D. Little, Inc.

d) Air dried.

e) Settled.

f) M=mine disposal tests, O=ocean disposal tests, B=used for both mines and ocean tests.

A systematic study of the effect of these species and the effect of ionic strength on the solubility of calcium sulfite in synthetic groundwaters was carried out. The concentrations were selected such that they cover typical concentrations in naturally occurring groundwaters. Acidic conditions were not included in this series of tests.

The measurement of the equilibrium sulfite concentration was made as described in Appendix B. A 0.5% slurry concentration of waste was prepared under nitrogen atmosphere using prewashed DA2 (clean) and L2 (filter cake, clean) with the test solution. Samples were taken after 1, 2, and 3 hours of stirring to ensure that equilibrium had been reached.

The sulfite concentration in the original remaining liquor in the waste was determined by reslurrying the sludge (15 g) with distilled water (7 ml) in a 15 ml centrifuge tube. The tube was sealed, shaken for 30 minutes, centrifuged, and a sample of the supernatant analyzed.

The initial conditions were chosen such that the following effects could be understood:

Experiment 1: Solubility in relatively soft water,
2: Effect of increased ionic strength,
3: Effect of varying $[Ca^{++}]$,
4: Effect of different waste,
5: Effect of varying Mg^{++},
6: Effect of added $SO_4^{=}$.

2. Results and Discussion

There was no significant difference between the sulfite levels in the liquor samples taken after 1, 2 and 3 hours, indicating that equilibrium had been reached within one hour. This is also in agreement with the results obtained in the dissolution data in the ocean disposal laboratory studies (Appendix B) where saturation had been reached within 1 hour. The initial experimental conditions and final equilibrium concentration of the various species of interest are summarized in Table A-2.

The results indicate that an increase of 80 - 200 ppm $[(2\text{-}5) \times 10^{-3}$ moles/liter] of calcium occurred in all cases due to dissolution of soluble salts present in the waste. However, the increase in $SO_3^{=}$ was only $(3.8 - 9.0) \times 10^{-4}$ M. In the cases of DA2 material (Experiments 1,2,3,5,6) the pH of the final solution was very high. This suggests the presence of $Ca(OH)_2$ (or NaOH) in the waste and may account for some of the extra dissolved Ca^{++}. The lower final pH of the L2 slurry (Experiment 4) suggests that in this case the extra calcium source was $CaSO_4$. The high pH of the final solutions obtained with DA2 material evidently caused precipitation of the magnesium as $Mg(OH)_2$ ("Ksp" = 1.2×10^{-11}) in all the experiments where DA2 material was used. The results of the

TABLE A-2

SOLUBILITY OF $CaSO_3$ IN SYNTHETIC MINE WATERS

		Initial Conditions[a]			Equilibrium Conditions					"Ksp" =
Exp. No.	Waste	$[Ca^{++}]$	$[Mg^{++}]$	Ionic Strength	$[Ca^{++}]$	$[Mg^{++}]$	pH	$[SO_3^{=}]\times 10^4$	Ionic Strength	$(Ca^{++})(SO_3^{=})$
1	DA2	6 ppm	2.2 ppm	0.0014 M	115 ppm	0.1 ppm	11.20	3.8 M	0.011 M	1.0×10^{-6}
2	DA2	6	2.2	0.0214[b]	121	0.5	11.23	9.0	0.032	2.7×10^{-6}
3	DA2	234[c]	2.7	0.0172	342	0.4	--	3.8	0.028	3.2×10^{-6}
4	L2	234[c]	2.7	0.0172	318	3.0	8.0	4.2	0.027	3.3×10^{-6}
5	DA2	8	34[d]	0.0099[e]	204	0.1	--	6.0	0.023	3.1×10^{-6}
6[f]	DA2	12	2.0	0.0107[e]	150	0.4	--	8.0	0.024	3.0×10^{-6}

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a) All solutions contain 11 ppm Na^+, 59 ppm HCO_3^- at initial pH = 7.
b) Added as 0.02 M $NaClO_4$.
c) Added as $Ca(ClO_4)_2$.
d) Added as $Mg(ClO_4)_2$.
e) Also contains $NaClO_4$.
f) Contains 300 ppm SO_4 added as Na_2SO_4.

Source: Arthur D. Little, Inc.

experiment with L2 material (Experiment 4) support this conclusion, since no magnesium was precipitated when the hydroxide concentration was much lower.

A comparison of DA2 and L2 samples under similar conditions (Experiments 3 and 4) gave similar results for "Ksp", $[SO_3^{=}]$, and $[Ca^{++}]$, suggesting that a pH variation between 8 and 11 at similar ionic strength does little to affect the soluble sulfite concentration. Similarly, the presence of 0 - 300 ppm of soluble sulfate (Experiments 5 and 6) had little effect on the soluble sulfite concentration under conditions where both the calcium concentration and ionic strength are fixed. The precipitation of most of the Mg in Experiment 5 prevents the assessment of its effect in these experiments. Variation of the calcium concentration in the range 121 - 342 ppm (Experiments 2 and 3) under conditions of similar ionic strength gave a variation of soluble sulfite close to that predicted from the $(Ca^{++})(SO_3^{=})$ = "Ksp" product. An approximately three-fold increase in the "Ksp" is observed when the ionic strength is increased about three-fold (Experiments 1 and 2), using $NaClO_4$ in the 0.01 - 0.03 M region.

Confidence in the equilibrium "Ksp" product at 0.03 M ionic strength is obtained from the values obtained for DA2 and L2 waste (Experiments 3 and 4) since no variation in this value should be obtained by using different materials.

At the extreme condition where all of the more soluble calcium salts have leached out and the material is more like pure $CaSO_3$, the soluble sulfite levels will be defined by the "Ksp" value at the ionic strength and composition of the leached solution. For example, for soft water containing no Ca^{++} and an ionic strength of 0.0014 M, we have

$$[SO_3^{=}]_{aq} = 1.0 \times 10^{-3} \text{ and } [Ca^{++}]_{aq} = 1 \times 10^{-3}; \quad [Ca][SO_3^{=}] = Ksp = 1 \times 10^{-6}.$$

The results obtained for the calcium and sulfite concentrations in the liquid phase of the as-received sludge materials are presented in Table A-3. The relationship of these numbers which were analyzed from samples which were at least 4 months old to the actual concentrations which existed in the freshly discharged material is uncertain, since oxidation of the sodium sulfite could have occurred. The "Ksp" values of $(5 \pm 2) \times 10^{-5}$ are slightly larger than expected for the L2 waste. Based upon an approximated "Ksp" curve for $CaSO_3$ in Na_2SO_4/Na_2SO_3 media (see Chapter III) and the ocean testing results, one would predict an ionic strength in the 0.5 - 1.0 M range for the L2 solution liquors. This ionic strength appears larger than the maximum possible value calculated assuming that the Na^+ and Mg^{++} content of the dried L2 solids is derived from soluble sulfate and sulfite salts in the liquor. However, ionic strengths in the range of 0.5 - 1.0 M are consistent with total liquor TDS levels for the DA2 material.

TABLE A-3

RESULTS OF ANALYSES OF WASTE LIQUORS

Waste	$[SO_3^{=}]$	$[Ca^{++}]$	"Ksp"
L1	4×10^{-3}	1.7×10^{-2}	6.8×10^{-5}
L2	2.2×10^{-3}	1.9×10^{-2}	4.2×10^{-5}
DA2	3.1×10^{-3}	2.2×10^{-2}	6.8×10^{-5}
DA3	1.6×10^{-2}	4×10^{-3}	6.4×10^{-5}

Source: Arthur D. Little, Inc.

3. Summary and Conclusions

The experimental results obtained in this study lead to the following conclusions:

1) The soluble sulfite level that may be expected due to displacement of the original remaining liquor depends on the waste material and its handling prior to dumping.

2) The long term equilibrium sulfite levels expected for neutral to basic conditions is 3.5 to 9.0×10^{-4} moles/liter (∿30 - 70 ppm).

3) The largest single influence on the soluble sulfite levels at constant $[Ca^{++}]$ concentration and under neutral to basic conditions is expected to be the ionic strength.

4) Under conditions of fixed ionic strength, variations in calcium levels will give the largest variability in soluble sulfite following the "Ksp" product.

5) No conclusions about the presence of Mg^{++} at pH lower than 11.2 can be made.

B. REACTION OF SULFITE-RICH WASTE WITH SYNTHETIC ACID MINE DRAINAGE WATER

1. Description of Experiments

Interaction of sulfite-rich waste with acid mine drainage (AMD) could lead to evolution of gaseous SO_2 which could be hazardous to personnel in the vicinity of the disposal operation or have other adverse environmental effects. The reaction may be described by the following overall equations:

$$2\ CaSO_3 + H_2SO_4 \rightarrow Ca(HSO_3)_2 + CaSO_4 \qquad (1)$$

$$Ca(HSO_3)_2 + H_2SO_4 \rightarrow 2H_2SO_3 + CaSO_4 \qquad (2)$$

$$H_2SO_3 \rightleftarrows H_2O + SO_2\uparrow \qquad (3)$$

$$\text{Overall: } CaSO_3 + H_2SO_4 \rightarrow CaSO_4 + H_2O + SO_2\uparrow \qquad (4)$$

The quantity and rate of SO_2 evolution would presumably depend on several factors. The extent of reactions (1) and (2) occurring would largely depend on the acid concentration and the alkalinity of the wastes. The release of SO_2 via reaction (3) is dependent on the total concentration of H_2SO_3 in solution and the atmosphere above/within the waste deposit. Since the conditions under which the waste would react with the acidic mine water are variable with respect to groundwater conditions and waste properties, a series of experiments was conducted to determine the effect of the following on the amount of SO_2 evolved:

a) total acid concentration
b) initial and final pH of reaction medium
c) reaction time
d) mixed (agitated) versus quiescent system
e) surface area changes.

The composition of four classes of acid mine drainage are given below.

	pH	Acidity*	Fe^{II} mg/l
Class I	2 - 4.5	1000 - 15,000	500 - 10,000
Class II	3.6 - 6.6	0 - 1000	0 - 500
Class III	6.5 - 6.8	0	0
Class IV	6.5 - 8.5	0	50

*mg of $CaCO_3$ needed to neutralize 1 liter of sample

Of these, Class I acid mine water with pH = 2 and acidity corresponding to 15,000 mg of $CaCO_3$ would be expected to yield the most SO_2 evolution and was used as a basis for preparation of synthetic AMD. Clearly no reaction should be observed for Class III and Class IV drainage since, at these pH regions, SO_2 is absorbed rather than evolved (e.g., FGC scrubber liquor).

Two different waste materials were used--direct lime scrubbing waste (L2) and dual alkali waste (DA2). Both wastes were prewashed prior to use in order to focus on $CaSO_3$ dissolution and SO_2 evolution.

The experimental apparatus for measuring the amount of SO_2 evolved consisted of a 3 necked round bottom flask (100 and 1000 ml) equipped with two gas syringes (0.5 and 2 liter capacity) connected to two of the necks. A typical experiment was conducted as follows: The syringes and space above the deoxygenated synthetic acid mine drainage test solution were filled with known amounts of N_2. The reaction was initiated by addition of a known amount of waste and the system sealed. The slurry was stirred for only 2 seconds to obtain a homogeneous sample. Synthetic acid mine drainage was prepared by mixing standard solutions of iron sulfate and sulfuric acid to the desired final pH. The SO_2 released in the system was continually mixed with the nitrogen by flushing the gas from one syringe to another above the surface of the reacting slurry. A sample of the gas mixture was taken and analyzed for SO_2 using a gas dector tube (Gastec, Ecology Controls, Inc.) capable of measuring 2 - 200 ppm of SO_2.

Two types of experiments were performed -- one step tests in which the reaction was allowed to continue for 25 - 45 minutes after which the amount of SO_2 generated was measured; and a second set in which SO_2 evolution was monitored with time as the pH of slurry increased. The total amount of SO_2 evolved in each of these types of experiments is not directly comparable. In the second set of experiments, the atmosphere above the slurry was flushed intermittently, thereby reducing the SO_2 partial pressure and potentially allowing more SO_2 release.

2. Results and Discussion

Table A-4 summarizes the experimental conditions and results of the one-step batch tests. The results show the importance of pH on SO_2 release -- as expected, the lower the pH, the greater the SO_2 evolution. With low acidity water (pH > 3), little or no SO_2 was produced. With highly acidic waters (pH ≈ 2), as much as 0.2 ml of SO_2 was produced per gram of dry solids.

Agitation of the slurry greatly reduced the SO_2 release. This can be attributed to a fast overall increase in pH of the slurry suppressing $CaSO_3$ dissolution. When the slurry was not agitated, only a small fraction of the total alkalinity in the waste was initially exposed to the water in the vicinity of the waste. Therefore, calcium sulfite was dissolved before the overall liquor pH increased, and the sulfite/bisulfite diffused to the more acidic surrounding water from which SO_2 was offgassed.

It can also be deduced from these experiments that, the lower the waste-to-water ratio, the greater the potential for SO_2 evolution (Experiments 1 and 3). With less waste there would be less alkalinity present, and more of the calcium sulfite could dissolve and SO_2 evolve before the pH of the water increased sufficiently to stop dissolution/offgassing.

Table A-5 summarizes the experimental conditions and results of the three tests where SO_2 release was monitored with time. Conditions for each test were varied to examine the effects of waste types and surface area.

With the as-received materials, all of the SO_2 was released during the first 15 minutes of the test before the overall liquor pH increased to above 2.5. The total amount of SO_2 released with the dual alkali waste was comparable to that produced in the one-step test starting at a slightly lower pH (Experiment 2) and was about 3 times that produced in the one-step test starting at the same pH (Experiment 1). Part of the difference in the SO_2 release between Experiments 1 and 8 can be attributed to uncontrolled variability in the experiments (e.g., degree of initial agitation); however, the repeated purging of the atmosphere above the slurry in Experiment 8 certainly contributed to the greater SO_2 evolution.

A direct comparison between the dual alkali and direct lime scrubbing wastes cannot be made from the results of this second set of experiments because of differences in solids concentrations used. However, the effects of differences in wastes can be seen by comparing the results of Experiment 9 with the results of Experiment 3. Both of these tests were performed at about the same solids levels, ∿0.12 wt.%. The dual

TABLE A-4

ONE-STEP SO_2 EVOLUTION STUDIES - TOTAL RELEASE

			Acid Water				Reactions Conditions			SO_2 Released		
Experiment	Condition/Variation	Waste	$[Fe^{+2}]$ (ppm)	pH	Wt.% Slurry	TOS Present (mmols added)	Agitation	Duration	Final pH	Total ml	ml/ Dry gm	% of TOS
1	High Acidity - Base Run (No Stirring)	DA2	11,000	2.1	0.25	1.5	Not Stirred	30 Mins.	2.9	0.022	0.09	0.07
2	- Longer Time/Lower pH	DA2	11,000	2.0	0.25	1.5	Not Stirred	40 Mins.	2.8	0.056	0.22	0.17
3	- Less Waste	DA2	11,000	2.1	0.13	0.8	Not Stirred	30 Mins.	2.6	0.018	0.14	0.10
4	- Agitation	DA2	11,000	2.1	0.25	1.5	Stirred	30 Mins.	4.6	<0.002	<0.01	<0.01
5	Low Acidity - Base Run (No Stirring)	DA2	560	3.6	0.25	1.5	Not Stirred	45 Mins.	3.8	<0.001	<0.01	<0.01
6	- Less Waste	DA2	560	3.4	0.05	0.3	Not Stirred	25 Mins.	3.65	<0.001	0.01	~0.01
7	- Different Waste (Stirring)	L2	560	3.7	0.05	0.3	Stirred	30 Mins.	6.2	Not Detected	--	--

Source: Arthur D. Little, Inc.

TABLE A-5

STUDIES OF SO_2 RELEASE VS. TIME (UNSTIRRED)

Experiment	Waste	Acid Water		Slurry	TOS Present (mmoles)	Time (min)	Cumulative SO_2 Release			pH
		$[Fe^{+2}]$,ppm	pH				Total ml	ml/dry gm	% of TOS	
8	DA2	2,000	2.1	0.25	1.5	3	0.020	0.08	0.06	--
						10	0.045	0.19	0.13	--
						16	0.060	0.25	0.18	--
						32	0.060	0.25	0.18	2.9
9	L2 (as rec'd)	2,000	2.0	0.12	0.75	3	0.020	0.17	0.12	--
						8	0.023	0.19	0.13	--
						15	0.026	0.22	0.15	--
						30	0.026	0.22	0.15	2.6
10	L2 (ground)	2,000	2.0	0.12	0.75	5	0.031	0.26	0.18	--
						40	0.045	0.38	0.27	--
						90	0.056	0.47	0.33	--
						135	0.056	0.047	0.33	--
						200	0.056	0.47	0.33	2.8

Source: Arthur D. Little, Inc.

alkali waste produced less SO_2 in 30 minutes than was produced with the direct lime waste in 3 minutes. This can be attributed to the slightly higher alkalinity of the dual alkali waste.

Interestingly, the ground direct lime scrubbing waste with roughly three times the surface area produced much more SO_2 than the as-received material and continued to produce SO_2 for a longer time and at slightly higher pH's. While it is not unexpected that the ground sample could produce more SO_2 (more surface and low alkalinity), the reason for the continued evolution of SO_2 at higher pH's with the direct lime scrubbing sample (and the dual alkali sample) than with the as-received sample is not fully understood. It may be due to (partial) incapsulation of direct lime waste particles with calcium sulfate, which is relatively insoluble at pH's in the range of 2.5-3.0. If this were the case, grinding the sample would expose more sulfite for dissolution. Analyses of the wastes do show the direct lime waste contains more sulfate ($\sim$20 mol % of the $CaSO_x$) than the dual alkali waste (less than 15 mol % of the $CaSO_x$). The difference is not large, but it is significant, especially in light of differences in the way in which the solids are produced in direct lime and dual alkali wastes which may allow more gypsum formation in the direct lime system.

3. Summary and Conclusions

1) Conditions conducive to SO_2 release from sulfite-rich FGC wastes are:

    - high contact water acidity;
    - low waste alkalinity;
    - low waste-to-water ratios; and
    - poor mixing of waste and water.

2) Very little SO_2 evolution would be expected with acidic wastes having pH's above about 3.0.

3) With highly acidic water (pH $\simeq$2.0), most of the SO_2 is evolved during initial periods of contact when the overall pH of the liquor is low (less than about 2.6).

4) Under the worst conditions tested (low alkalinity waste, ground to high surface area; low waste-to-water ratio; an initial water pH of 2.0; and no agitation), the amount of SO_2 released amounted to 0.33% of the total TOS present. This would correspond, for this waste, to about 470 liters (0.47 M^3) per dry metric ton of waste.

C. FREEZING POINTS AND PHYSICAL PROPERTIES OF FROZEN AND THAWED FGD WASTE

1. Discussion of Experiments

The possibility of waste dewatering upon freezing and thawing was investigated to determine the potential for release of occluded liquor during storage of the material under extreme weather conditions. Experiments were designed to examine the difference in the ability of frozen and thawed waste to retain water under conditions where the waste is stored loosely, packed and after reslurrying with water.

Four different waste materials were tested: two dewatered wastes from a direct lime scrubbing system--one without ash (L2) and one with ash (L1); thickened waste containing ash from a direct limestone scrubbing system (LS1); and a dual alkali waste without fly ash (DA2).

Freezing points for two direct scrubbing materials (L1 and LS1) were first determined from cooling curves after immersion in a bath at -8°C. Dewatering characteristics were then evaluated. Both as-received samples and samples of the waste that were allowed to freeze for 3 days at two temperatures and then thawed for 3 days at room temperature were studied.

A fixed amount of waste (15 g) was placed in a Buchner funnel (4.5 cm diameter) equipped with filter paper (Whatman #1) and a flexible rubber dam. The rubber dam served to prevent air from passing through the sample and to exert a uniform pressure on the surface of the wet solid. Suction was applied for 10 minutes and the amount of water released was measured by weighing the receiving flask before and after suction. The percent solids remaining after suction was applied was also measured as a check on the dewatering characteristics.

2. Results and Discussion

The freezing point of L1 waste was determined to be -1.0°C. This freezing point would correspond to the freezing point of a 0.25 M Na_2SO_4 solution. Substantial supercooling was observed (to -4°C) before the sample froze as one hard mass. The freezing point of the LS1 waste was found to be -0.5°C. This would correspond to a solution concentration of ~0.11 M Na_2SO_4. Both the frozen samples contained many crystallization lines, again indicative of very rapid freezing due to supercooling. The results of the dewatering experiments for the waste samples exposed to various conditions are given in Table A-6. Samples of the dual alkali waste were frozen both as packed samples (packing density = 1.4 g/cc) and as loose samples (0.76 g/cc). All the packed samples froze, yielding a hard mass, while the loose sample was able to be pried apart with a spatula. Upon freezing and thawing of all the as-received samples, no appearance of a liquid layer on the surface was observed.

TABLE A-6

SUMMARY OF FREEZE/THAW EXPERIMENTS

Waste Material	Percent Solids			
	As Received	As Received/Suction	-24°C → 20°C/Suction	-8°C → 20°C Suction
L1	65.7	70.6	68.4	71.1
L2	55.1	58.4	71.1[a]	59.4
LS3	57.8	68.5, 67.8	--	71.7
DA2 (loose packed) 0.76 g/cc	61.9	64.10	63.9	63.7
DA2 (hard packed) 1.4 g/cc	61.9	64.10	--	63.3
DA2 (water added) (3 g H_2O + 30 g waste)	59.0	64.10	--	71.8

Waste Material	Amount of Liquid Extracted (g) from 15 g Sample[a]		
	As Received/Suction	-24°C → 20°C/Suction	-8°C → 20°C/Suction
L1	0.6	--	0.5
L2	0.7	0.65	0.6
LS3	1.7	1.45	1.45
DA2 (loose)	none	--	none
DA2 (hard)	none	none	none
DA2 (water added)	1.5 (Calculated based on added amount & result for above)	--	1.75

---

[a] Does not include amount of water retained by filter paper. Average value calculated 0.33 g.

Source: Arthur D. Little, Inc.

The results in Table A-6 indicate that no substantial difference in dewatering characteristics occurs upon one freeze/thaw cycle (at -24°C or -8°C) (room temperature) for all the samples except the DA2 sample to which water had been added. The amount of water released after the freeze/thaw cycle, in this case, was higher than from as-received samples, and this is corroborated by the percent solids remaining. In all of the other cases, the amount of water released and percent solids after the freeze/thaw and suction were similar to the values obtained for samples which were not frozen.

3. Summary and Conclusions

1) No significant change in dewatering characteristics of dewatered sulfite-rich wastes occurs during one freeze/thaw cycle.

2) Waste samples would be expected to freeze in the 0 to -3°C range depending primarily upon the salt content of the liquor occluded with the solids.

3) Addition of water to a waste followed by freeze/thaw may cause a change in dewatering characteristics.

4) As expected, loosely packed waste which has frozen is much more susceptible to breaking apart than hard packed material. Thus, loosely packed frozen material may be workable with a front-end loader.

APPENDIX B

OCEAN DISPOSAL LABORATORY STUDIES

To permit a more complete evaluation of the environmental impact of disposal of FGC wastes in the oceans, laboratory studies were conducted to generate information on the following phenomena for which adequate data could not be found in current literature:

1) Characteristic suspended solids levels due to simulated ocean dumping of the various wastes;

2) The current velocities required to erode benthic waste deposits;

3) The rate of dissolution of sulfite from sulfite-rich wastes and the maximum final concentration to which potentially toxic sulfite would rise; and

4) Effect of the resultant dissolved sulfite on the available dissolved oxygen concentration.

The approach taken to investigate potential impacts of waste in each of these areas and a description of the experimental studies are presented in this Appendix. Table B-1 provides compositions of the waste samples.

A. SIMULATED DROP TESTS

1. Description of Experiments

In order to provide additional information on the behavior of FGC wastes during descent in a water column, laboratory-scale drop tests were conducted. Although extreme differences are expected to exist between actual dumping at sea and these laboratory experiments, insights concerning breakup and extent of erosion during descent (suspended solids level) and behavior of the resultant plumes were obtained from the laboratory tests. The experiments described below were directed at understanding the effects of variations in: a) waste types; b) amounts of dropped waste; and c) cohesiveness as represented by different moisture contents and compaction.

The simulated drop tests were conducted in a 20-gallon aquarium (36" high x 12" x 12") filled with synthetic seawater ("Instant Ocean").® Waste samples of various sizes were dropped from a plastic container which had a removable sliding bottom. The container was fitted with side extensions which enabled the device to hang such that the sliding bottom was immersed in the water column. Turbulence in the water column was achieved by using a steel screen (9" x 9", 1/4" mesh) mounted on a rigid rod. A typical drop was performed as follows.

TABLE B-1

MAJOR CONSTITUENTS OF FGC WASTE SAMPLES FOR THIS PROGRAM

System	Sample Designation	Form	Type	Simultaneous Ash Removal	Wt % Solids[a]	Chemical Analysis (mmols/gm-dry) Ca	Mg	Na	TOS[b]	SO_4	Cl	Wt% Acid Insolubles	Use in Disposal Testing[f]
Dual Alkali	DA1	Filter Cake	Sulfite-Rich	No	54	7.15	0.25	0.43	5.60	0.97	0.04	0	O
	DA2[c]	Filter Cake	Sulfite-Rich	No	63	-	-	-	5.88	-	-	-	B
	DA3	Filter Cake	Sulfite-Rich	Yes	57	4.45	0.22	0.22	2.66	0.87	0.03	31	B
	DA4	Filter Cake	Sulfite-Rich	No	98[d]	7.41	0.14	0.21	5.11	1.28	0.02	3	--
Direct Lime	L1	Centrifuge Cake	Sulfite-Rich	Yes	63	4.59	0.05	0.03	3.85	0.70	0.05	35	B
	L2	Filter Cake	Sulfite-Rich	No	52	7.22	0.07	0.03	5.76	1.37	0.03	1	B
	L3	Filter Cake	Sulfite-Rich	No	47	6.99	0.23	0.02	5.89	0.52	0.01	3	O
Direct Limestone	LS1	Filter Cake	Sulfite-Rich	Yes	57	6.48	0.07	0.03	3.04	0.64	0.09	25	--
	LS2	Filter Cake	Sulfate-Rich	Yes	79	4.20	0.04	0.03	0.01	3.69	0.05	38	--
	LS3	Thickener Underflows	Sulfite-Rich	No	59[e]	7.06	0.07	0.03	5.24	0.99	0.05	6	M
ACS Scrubbing	G1	Centrifuge Cake	Sulfate-Rich	No	83	6.05	0.01	0.02	0.00	6.04	<0.01	< 1	O

---

a) As received.

b) Total Oxidizable Sulfur ($HSO_3^- + SO_3^=$).

c) Insoluble in 1 molar HCl.

d) Air dried.

e) Settled.

f) M=mine disposal tests, O=ocean disposal tests, B=used for both mines and ocean tests.

Source: Arthur D. Little, Inc.

To create turbulence, the steel screen was pulled through the seawater solution in about 2 seconds. This factor was introduced in a majority of the tests. The plastic device containing a known amount of waste was placed on the surface, and the waste was released by sliding the plastic bottom. In the cases where the sample did not drop of its own accord, it was forced to drop using a rod.

After the bulk solids had dropped to the tank bottom, samples of the water and entrained solids were obtained by rapidly (i.e., 7-10 seconds) drawing 1-liter portions through 6 mm diameter glass tube probes into vacuum filter flasks using suction. Two types of samples were obtained. First, immediately following the drop, a "plume follower" sample was obtained from that region in the water column through which the solids had passed (i.e., the "plume") and which appeared visually to have the highest concentration of suspended solids. Second, at fixed time intervals after the drop, samples were obtained from a point equidistant from the aquarium sides and approximately one-third the distance (10-12 inches) up from the bottom. The probe was placed at this point with the inlet pointed up in an effort to avoid suspended solids which resulted from impact of the bulk solids with the tank bottom and subsequent upwelling.

The suspended solids levels in the liquid were determined by filtration through a tared glass fiber filter (Reeve-Angel 934AH, 37 mm diameter). Quantitative transfer of all the solids was assured by using portions of the filtrate to wash the solids from the flask. The filter was weighted wet and after drying (85°C) to constant weight. The loss on drying corresponded to the amount of water retained by the filter and allowed calculation of the amount of dissolved solids remaining on the filter due to the entrapped "seawater." The amount of suspended solids collected was calculated by subtracting the weight of dissolved solids contributed by the seawater from the total weight gain of the dried filter. Uncertainties in weights and transfers were estimated to be approximately 5 mg.

The waste samples used in these tests represented two different categories of bulk properties:

- loose, noncohesive moist solids represented by the as-received dual alkali and gypsum filter cakes; and
- cohesive wet solids represented by the direct lime scrubbing wastes.

In addition, tests were conducted on portions of the loose, noncohesive solids whose properties had been modified either by compacting alone or by rewetting prior to compacting.

2. Results

A summary of the experiments performed and their results is presented in Table B-2. Generally, it was observed that the loose, drier materials (dual alkali and gypsum) tended to fall apart during the drop (i.e.,

TABLE B-2

RESULTS OF FGC WASTE DROP TESTS

	Waste			Drop Specimen				Suspended Solids (mg/1)[a]		
Test Series	Process	Sample Code	% Solids	g. wet	Dimensions (inches)	Density g/cc	Turbu-lent	Plume Follower[b]	1 min	3 min
C-1	Dual alkali	DA1	54	10	1 x 1 x 1	∿0.6	--	--	--	10
C-2	"		54	20	1 x 1 x 1	∿1.2	--	45	--	5
C-3	"	"	54	20	1 x 1 x 1	∿1.2	yes	75	--	25
			(Broke into 4-5 pieces during descent)							
C-4	"	"	"	20	1 x 1 x 1	∿1.2	yes	25	--	15
			(Dropped as single lump)							
D-1	"	"	"	200	4 x 3 x 1 (min 1 x 1 x 1)	∿1.2	yes	400	--	70 43 (5 min)
			(Broke into 4-5 pieces during descent)							
D-2	"	"	"	40		∿0.6	yes	--	100	
				4 more at 40g at 1 min intervals			--	--	--	--
									350(5 min),175 (7 min), 50(11 min)	
D-3	Direct Lime (rewetted)	L1	∿55	25	1 x 1 x 1	∿1.5	yes	<5	Not measurable	
D-4	Direct Lime (fly ash)	L1	∿63	25	1 x 1 x 1	∿1.5	yes	<5	Not measurable	

[a] Reported to nearest 5 mg/1

[b] Approximately 30 seconds after drop.

Source: Arthur D. Little, Inc.

TABLE B-2 (Continued)

RESULTS OF FGD WASTE DROP TESTS

Test Series	Waste	Sample Code	% Solids	Drop Specimen			Turbu-lent	Suspended Solids (mg/1)[a]		
				g. wet	Dimensions (inches)	Density g/cc		Plume Follower[b]	1 min	3 min
E-1	Dual alkali	DA1	54	200	(4x3x1)-$(1)^3$	~1.2	yes	240	130	75
E-4	Dual alkali (rewetted)	DA1	50	200	same	~1.2	yes	140	40	15
E-2	Direct lime	L2	52	200	same	~1.2	yes	15	5	<5
E-3	Direct lime	L1	66	200	same	~1.2	yes	10	5	<5
F-1	Gypsum	G1	80	200	same	~1.2	yes	55	20	5
F-2	Gypsum (rewetted)	G1	75	200	same	~1.2	yes	50	5	5
F-3	Direct lime	L3	50	200	same	~1.2	yes	40	15	10

[a] Reported to nearest 5 mg/1

[b] Approximately 30 seconds after drop

Source: Arthur D. Little, Inc.

tests C3, D1 and E1) whereas more cohesive materials (lime wastes) tended to drop as one large mass (i.e., tests E2, E3, and F3). These large masses would often fall in an oscillating motion which in some cases led to an impact with the walls of the aquarium. The drier solids were broken up into smaller lumps by the time they reached the bottom and would break up further after sitting on the bottom a short while. The more cohesive solids would remain somewhat more intact, but developed fissures and exhibited marginal slumping and erosion while resting on the bottom.

The amount of surface erosion and particle breakup during the drop as measured by the suspended solids level was much greater for the dual alkali solids (tests D1 and E1) than for any of the other samples. Under similar conditions no substantial difference was measured in the suspended solids levels after the L1, G1, L2 or L3 samples were dropped (tests D3, D4, and E2 through F3).

The suspended solids level was dependent on the mode of descent of a specific waste (one large mass versus several pieces--tests C3 and C4, D1 and E1) and to a lesser extent on quiet versus turbulent conditions (tests C2 and C3).

The water content and its relationship to the cohesive properties of the waste also affected the suspended solids level. Further wetting of a second sample of already cohesive material (L1--tests D3 and D4) did not create significantly different suspended solids levels after a corresponding drop. However, further wettings of second samples of less cohesive material (dual alkali--tests E1 and E4) resulted in a lower suspended solids level, which may be accounted for by the increased cohesiveness of the wetted material.

3. Summary

1) During descent through the test water column, cohesive FGC waste materials tend to remain intact or to break up into a relatively few large pieces. Noncohesive (or less cohesive) FGC materials tend to break up into many smaller pieces, even approaching disintegration.

2) The less cohesive material leaves higher suspended solids levels during and after a drop in the water column than the more cohesive wastes.

3) Compacting of less cohesive FGC materials tended to lower the suspended solids levels resulting from a drop through water.

4) For the less cohesive materials, rewetting followed by compacting resulted in a marked lowering of the resultant suspended solids levels.

B. BENTHIC EROSION STUDIES

1. Description of Experiments

As part of the assessment of the use of the ocean as a disposal option for FGD waste, waste erodability studies were conducted at the New England Aquarium (NEA) for Arthur D. Little, Inc. The purpose of these experiments was to determine current velocities at which waste deposits would erode, the subsequent rate of erosion as a function of current velocity, and the manner of waste movement as bed load or suspended load. For an actual waste dump out of a bottom-dump barge, a portion of the waste will immediately be suspended in the water column and travel large distances under the action of currents and waves before being deposited. Large pieces of waste, however, may reach the bottom at the dump site. The NEA experiments were designed to determine the basic erosion type properties of individual wastes and, thus, to enable more accurate prediction of the movements of bottom accumulations of waste.

The waste samples tested, which include the most cohesive (hence presumably erosion-resistant) ones available, were direct lime centrifuge cake with fly ash (as received), direct lime filter cake without fly ash (as received) and dual alkali filter cake without fly ash (rewetted). The first two were considered cohesive based on the results of the drop tests described above. In addition, a series of tests was run on "Fall River mud," a dredged material. This series was run to correlate our experimental results and procedures with those of Nacci (1974), who ran similar tests on this mud, and to provide a basis for determining the behavior of waste after an actual ocean dump through comparison with the more well-known behavior of dumped dredged material.

The wastes studied were at water contents believed to simulate in-barge conditions. By investigating:

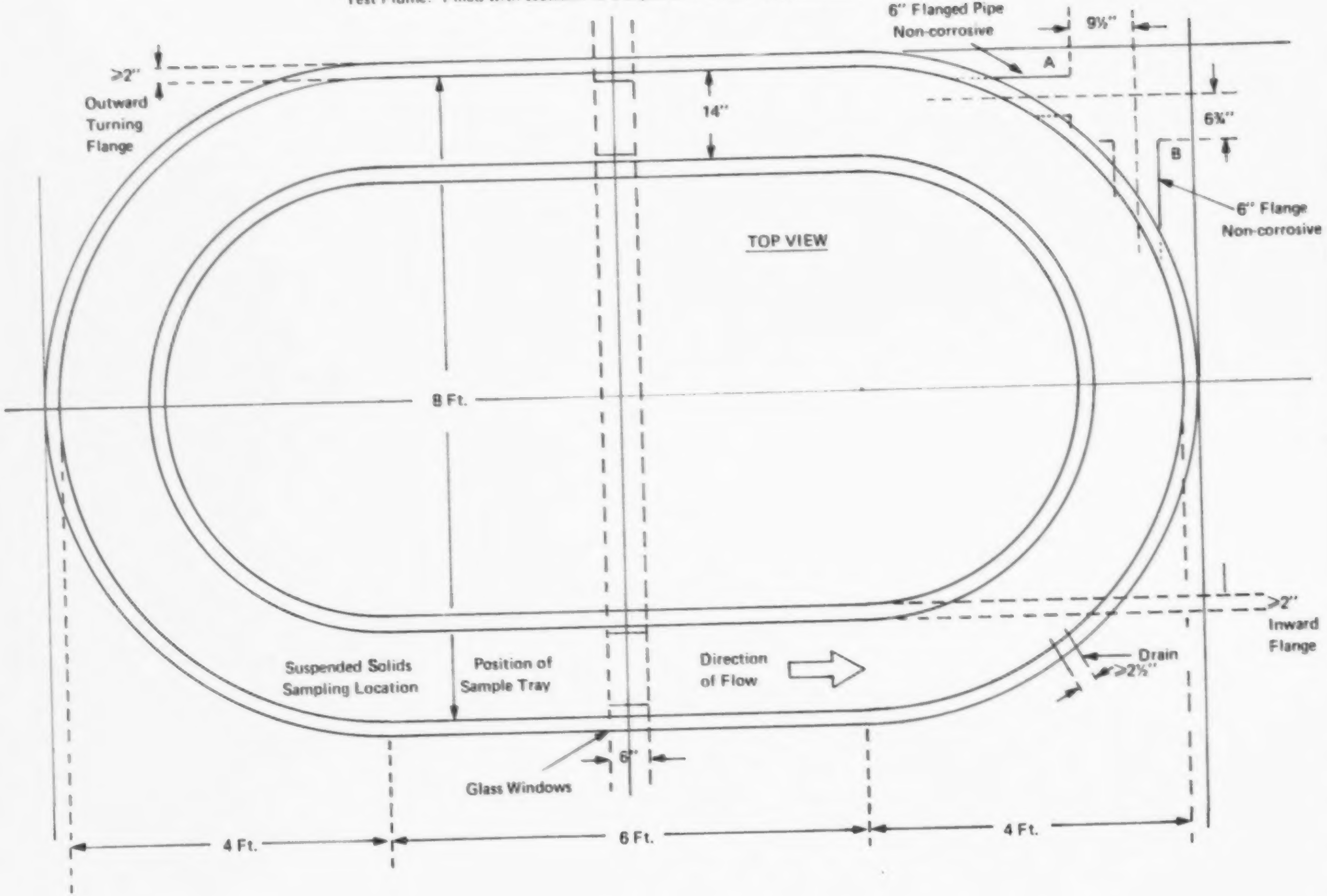
1) the variation of the water content of wastes on the ocean bottom with burial depth and with time,

2) the variation of erosion rates with water content for each waste, and

3) the possible variation of erosion rates with water properties (i.e., temperature),

a more accurate determination of waste movement on the ocean bottom would be obtained. In future erosion studies, replicate runs should be planned to obtain accurate average erosion rates. Additionally, solubility data should be known in order to interpret the results accurately.

All testing was conducted in seawater circulated in a 1,400-liter flume chamber shown in Figure B-1. The minimum mean mid-depth velocity obtainable with this apparatus is 13 cm/second; tests were run at velocities as high as 86 cm/second. The variation of water velocity from one section


Test Flume: Filled with seawater to a depth of ≈ 14 inches (1400 liters)

6" Flanged Pipe
Non-corrosive
9½"
A
>2"
Outward
Turning
Flange
14"
6¾"
B
6" Flange
Non-corrosive
TOP VIEW
8 Ft.
>2"
Inward
Flange
Drain
>2½"
Suspended Solids
Sampling Location
Position of
Sample Tray
Direction
of Flow
6"
Glass Windows
4 Ft.
6 Ft.
4 Ft.

Source: Arthur D. Little, Inc., and New England Aquarium.

FIGURE B-1 BENTHIC EROSION STUDY TEST APPARATUS of the flume to another was a peculiarity of this apparatus and influenced the test results. Most notably, velocities near the outer wall of the flume were 10-20% greater than the mean velocity and decreased in an approximately linear manner across the width of the flume. The pump generated turbulence; however, this turbulence seemed to dissipate quickly and was not observed near the sample.

The dredged material was packed into a pyrex tray 8" x 8" x 2", and the surface was rounded and smoothed. This pan was then placed in mid-flow, approximately 6" from the bottom of the flume as in Nacci's tests, and was allowed to sit for either 1 or 16 hours (overnight) before the test was run. In Nacci's experiments this mud exhibited evidence of bioturbation; however, the NEA samples were frozen while in storage and showed no such effects.

The FGC waste samples, on the other hand, were placed on a cookie sheet with a roughened surface. In each test, 700 grams of waste were well worked and molded onto the sample tray so as to form one continuous piece of waste 1/4-1/2 inch in depth, with a smooth surface visually similar to settled waste samples in the drop tests. This working resulted in the transformation of a pile of powdery or cakey waste into a solid, semi-liquid mass. The waste samples were placed at the bottom of the flume and extended the full width of the apparatus. This method of sample prepartion undoubtedly influenced the measured erosion rates. The cookie sheet, which exhibited some lift, was secured to the bottom of the flume with putty. When necessary, thin glass rods were also used to pin the edges of the tray to the bottom of the flume.

Samples were placed in the filled flume at zero water velocity with minimal sample disturbance observed. Both single and multivelocity tests were run; during multivelocity tests, water velocities were increased but never decreased, and the velocities were held constant when heavy sustained erosion was observed to occur. The velocities studied ranged from approximately 10-60 cm/second and covered the range from no erosion to heavy sustained erosion for each material. These tests generally lasted less than an hour during which as much as 50% by weight of the original sample was lost. The weight loss of the sample over the course of the test was measured, and suspended solids levels were measured frequently.

Suspended solids levels were measured either turbidimetrically or gravimetrically. Water samples for these measurements were obtained by submerging empty sample bottles into the flow immediately upstream of the sample just below mid-depth. Minimal sample disturbance was observed during this procedure. Scatter in the suspended solids measurements of a factor of 1.5 was not unusual and is considered to be due to the method of retrieving the water samples. The background turbidity measurements were subtracted out of the test measurements; however, it should be noted that in some tests these were of the same order of magnitude (1 ppm).

At the end of a test the pump was immediately shut off. The sample was removed when flow ceased, and the weight loss of the sample over the course of the experiment was determined. Minimal disturbance of the sample was observed during the removal procedure. For several experiments a control experiment was run at zero water velocity to determine the degree of possible water uptake by the sample.

2. Results and Discussion

The results of these experiments, both qualitative and quantitative, are summarized in the accompanying figures and tables.

The immediate quantitative result obtained is the erosion rate calculated from the sample weight loss. This quantity, defined as the rate at which mass is removed from the immersed sample per unit surface area per unit time, is a function of waste type, water content, and other waste properties and flow conditions. With the erosion rates of a waste determined for a variety of water contents and with proper dump site water column and substrate data, the rate of waste removal from a waste accumulation on the ocean bottom could be estimated.

A secondary quantitative result is the percent suspended load, defined as the percentage of eroded material traveling in the water column as determined from the final suspended solids measurements and total weight loss measurements. The percent suspended load could be useful in determining the extent of movement of eroded material; suspended waste will travel farther and faster than waste moving as bed load along the bottom.

Qualitative results obtained include observations of erosion type and transport type. Transport type, as discussed above, is either bed load or suspended load. Erosion type has been characterized as streamining or flaking. Streaming is said to occur when fine particles are continuously removed from all or a portion of the sample and stream upwards into the water column. Flaking occurs when bits of waste much larger than the particle size are loosened from the sample. Generally, streaming contributes to suspended load; flaking, to bed load.

The quantitative results obtained for erosion rates as summarized in Figures B-2 and B-3 did not duplicate well. The qualitative results, however, presented in Table B-3 are more clear. All the wastes displayed heavy and continuous erosion at velocities over 25 cm/second, with the dual alkali waste being the most easily eroded.

It is possible that the experimental setup was a principal source of errors in the erosion rates; however, the complex and statistical nature of the phenomenon could certainly have been a contributing factor.

It is possible that as much as 10-50% error was introduced into the calculated erosion rates as a result of the experimental setup. Since flow velocities varied (approximately) linearly acorss the width of the flume and erosion rates were highly nonlinear with velocity, observed rates were likely higher than those that would occur under uniform flow. Other factors may have also increased the error in the results.

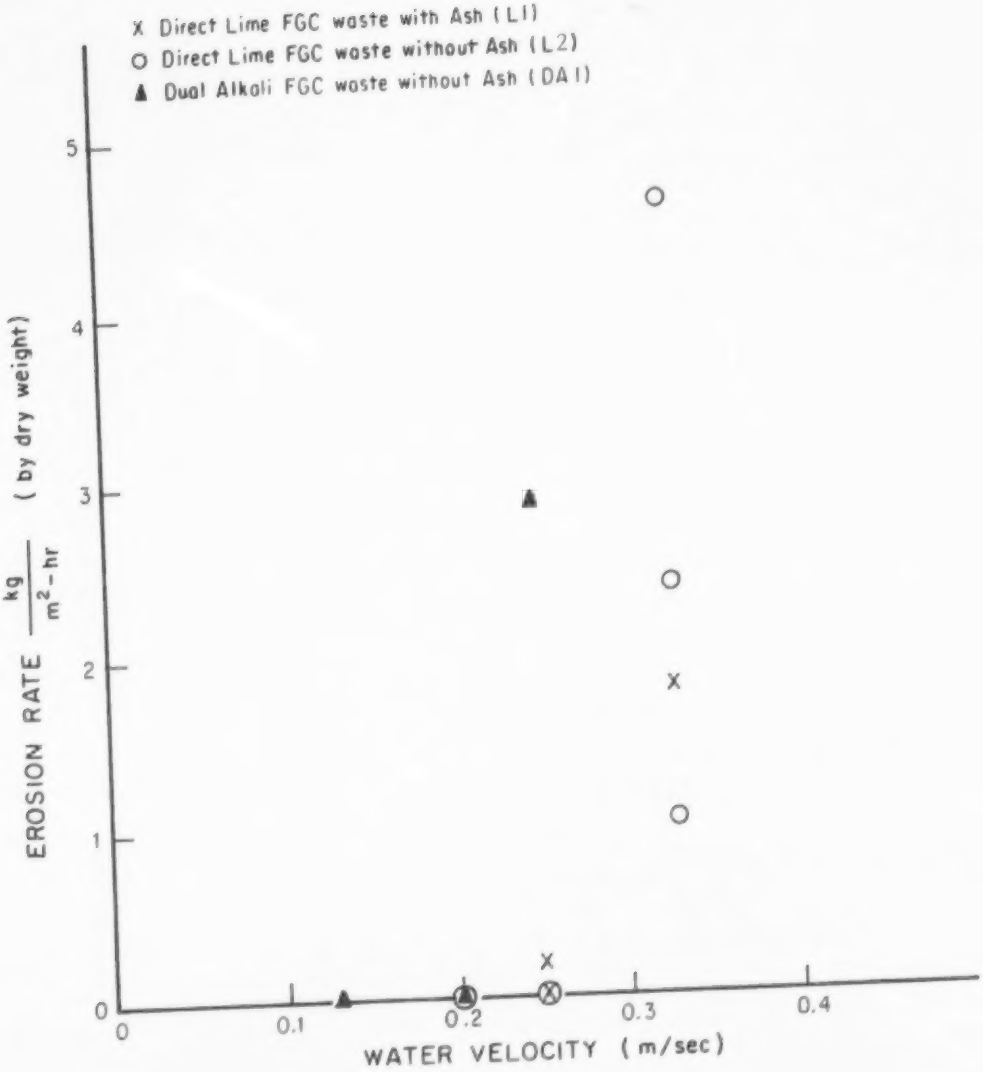
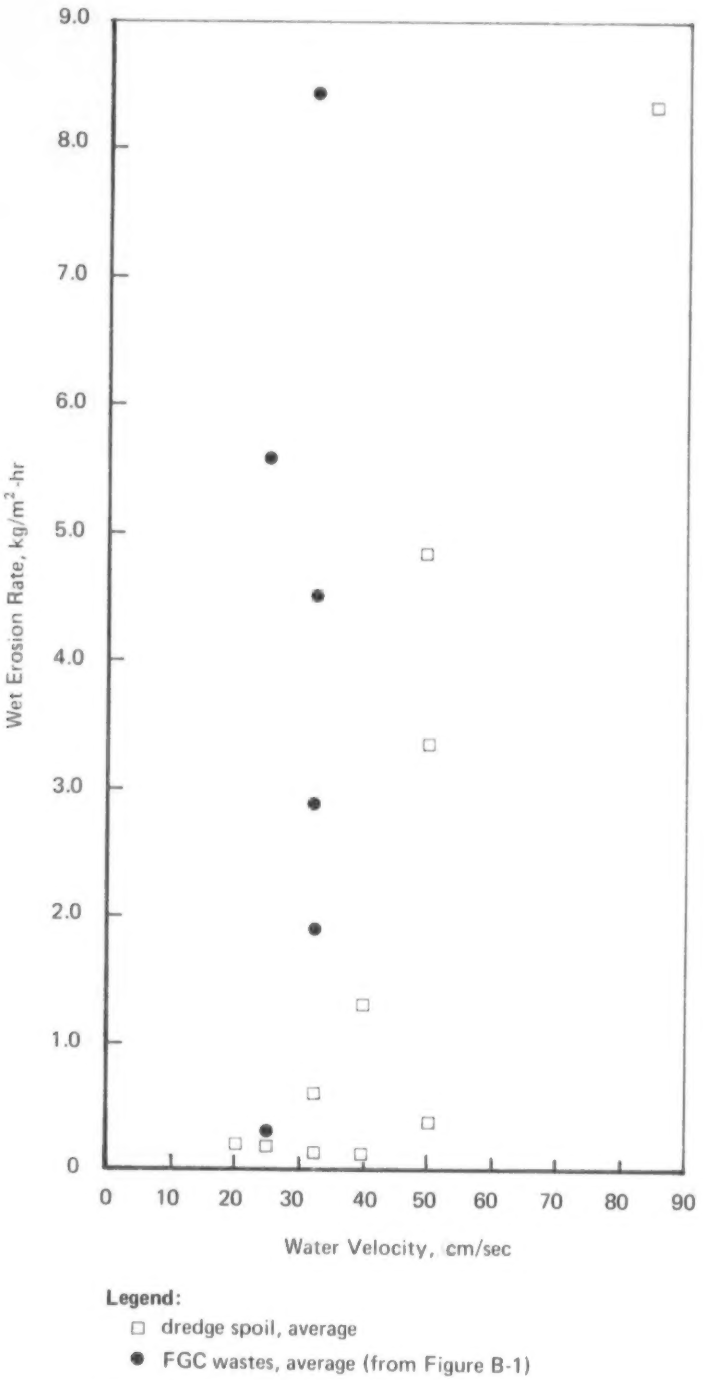


FIGURE B-2 OBSERVED EROSION RATES OF THREE FGC WASTES AS A FUNCTION OF WATER VELOCITY

Source: Arthur D. Little, Inc. and New England Aquarium



Source: Arthur D. Little, Inc. and New England Aquarium

FIGURE B-3 OBSERVED AVERAGE EROSION RATES OF FGC WASTES AND DREDGE SPOIL AS A FUNCTION OF WATER VELOCITY

TABLE B-3

SUMMARY OF QUALITATIVE RESULTS OF BENTHIC EROSION STUDIES

SAMPLE PROPERTIES			EROSION PROPERTIES		
Waste	% Solids	Propensity for Liquid Flow[a]	Erodability[b]	Type of Erosion	Observed Primary Method of Transport
L1	62-66%	xx	x	Streaming	Suspended
L2	54%	x	x	Streaming, Flaking	Suspended
DA1	52%	-	xx	Flaking, Streaming	Bedload
Dredged Material	ND	-	-	Streaming	Suspended

[a] Flow Propensity

Key: - = Does not flow
X = Flows
XX = Flows relatively easily

[b] Erodability

- = Relatively stable
X = Erodes
XX = Very erodable

ND - Not determined

Source: Arthur D. Little, Inc., and New England Aquarium.

Sometimes, however, waste was totally eroded away in the high velocity regions, causing a significant decrease in the actual erosion rate. The total effect cannot be determined and certainly varies from experiment to experiment.

Proper use of the calculated erosion rates is dependent upon an understanding of the erosion process. These rates are functions of the nature of eroding material and the immediate flow field. For a nonhomogeneous material whose properties vary with depth, the erosion rate will not be constant over the course of the experiment. Thus, the presoaked dredged material seemed to exhibit a decreasing erosion rate over the course of the experiment and sometimes erosion ceased altogether. The waste samples, on the other hand, were designed to be as homogeneous as possible. However, these samples commonly sat 15-20 minutes prior to testing. during which time slight inhomogeneities developed. The direct lime FGC waste samples developed an easily eroded surficial layer, whereas the surface of the dual alkali sample seemed relatively erosion-resistant.

Thus, the erosion rates calculated are properties of the given waste at its given water content. The variation of erosion rate with water content was not studied, although it is believed that for completely saturated wastes, higher water content would indicate higher mobility. Further studies along this line may be in order and should be accompanied by an investigation of waste water content after long-term settling.

Another observed phenomenon that influenced the measured erosion rate was the ability of the waste to flow slowly as a liquid, thus changing the surface area exposed to the flow. The dredged material did not flow; however, the direct lime waste with fly ash flowed fairly easily and increased its coverage of bottom area by approximately 15% over the course of a one-hour run. The direct lime waste without fly ash exhibited about two-thirds that expansion; the dual alkali sample barely flowed at all.

The errors induced in the measured erosion rates by the phenomena of liquid flow and velocity variation are, in general, small compared to the natural real variation of the erosion rate from one experiment to another. This variation is a result of the complex and statistical nature of the actual erosion process.

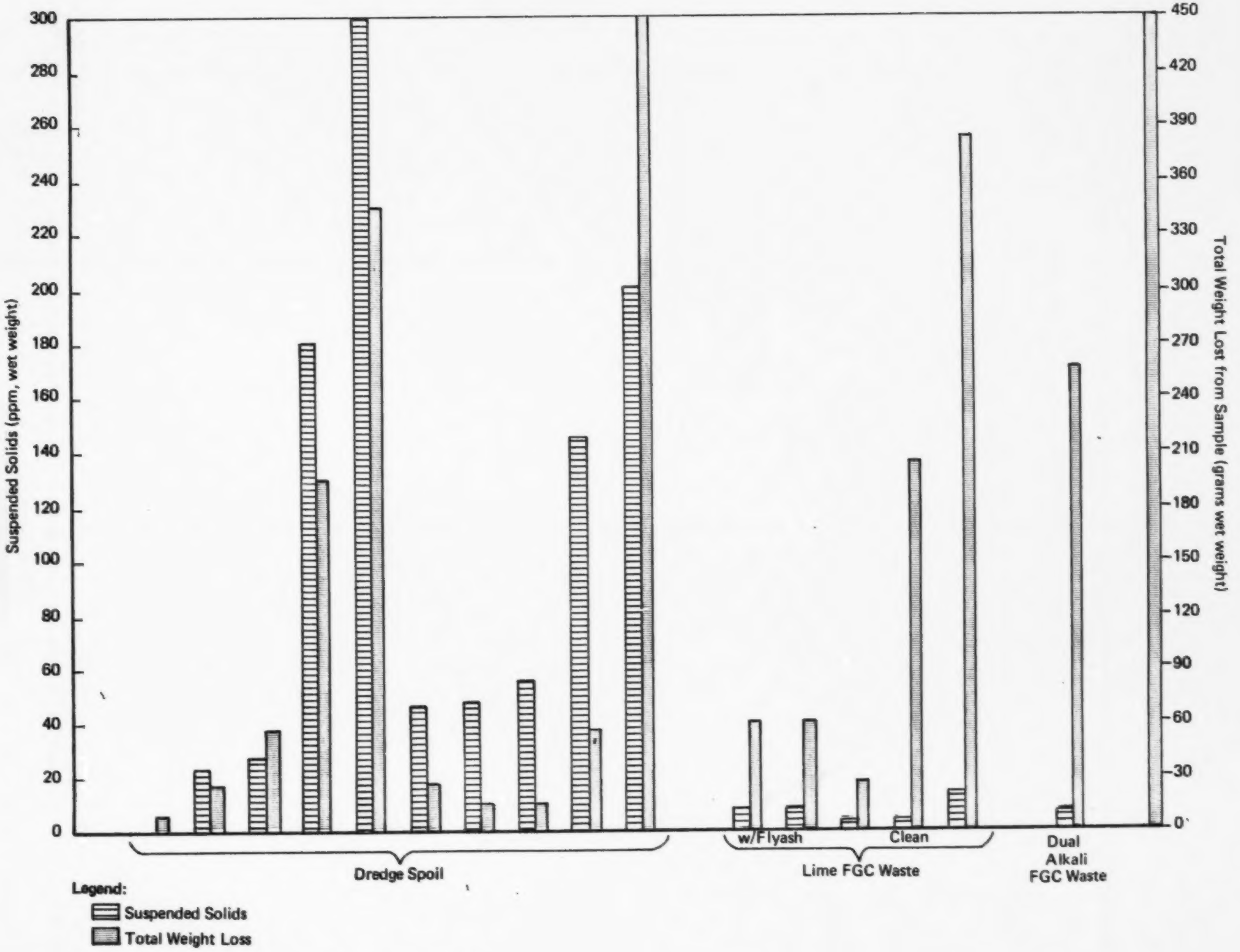
In general, the erosion occurring was not a steady streaming or flaking from the surface of the sample. It was observed that relatively light erosion occurred until local irregularities (holes or furrows) formed. This sometimes took 5-10 minutes. At this point, local scour near these irregularities strongly dominated any surface erosion. Sometimes furrows were extended by the flow of the entire length of the waste sample. Since the observed erosion was primarily due to local scour and no two samples, however similarly prepared, eroded in exactly the same way, it is expected that a variation in erosion rate will always be observed. In a replicate run of a lime filter cake without fly ash, the erosion rate doubled. Similar variation was observed for the dredged material.

An additional phenomenon, possibly affecting erosion rate measurements, is that of water uptake by the sample, resulting in misleading weight loss measurements. This phenomenon was observed only in the dredged material and the dual alkali sample. However, since the dredged material was presoaked and the dual alkali sample sustained very heavy erosion, this effect was considered minor except for certain dredged material runs sustaining only minor weight loss.

Anomolous results were obtained in the suspended solids levels. As can be seen in Figure B-4, suspended solid levels observed in the dredged material series were much higher than those observed in the waste series, even for comparable sample weight losses. One would expect, therefore, a relatively high observed bed load for the FGC wastes. With the exception of the dual alkali sample, however, only minor amounts of bed load were observed in the flume at the conclusion of the experiments. Dissolution is possibly the cause for the low suspended solids levels observed in the tests with the direct lime wastes.

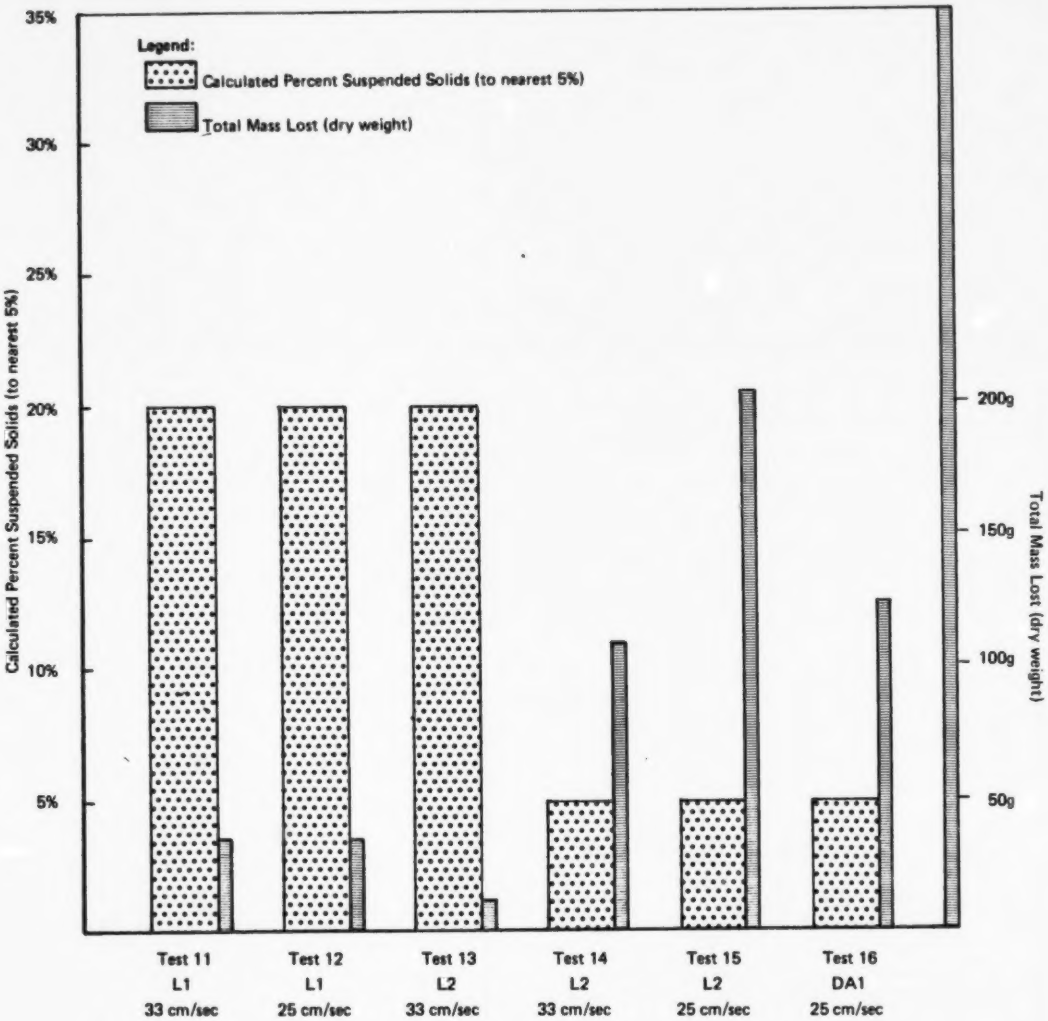
The possibility of water uptake by the sample and dissolution may also have caused some errors in the estimates of percent suspended load, obtained from weight loss and suspended solids (see Figure B-5). As a result of the errors in these measurements and the additional uncertainty as to whether the suspended solids measurement reflects the depth averaged concentration in the water column, the percent suspended load calculations might be considered accurate within a factor of 2-3 if it is assumed that no dissolution of samples occurred.

The solubility of these wastes had not yet been determined; however, the data obtained in this study indicate dissolution played a major role in the erosion of the direct lime wastes and was a possible factor in the erosion of the dual alkali waste. For similar sample weight losses the waste showed much lower suspended solids levels than the dredged material. Two conclusions can be drawn from this observation: either the waste dissolved or a large portion of it was traveling as bed load. Unfortunately it was impossible to obtain quantitative bed load measurements with this apparatus. However, due to the nature of the flow in the flume, bed load tended to accumulate in certain regions of the tank. These regions were generally associated with low flow velocities and included the juncture of the bottom with the inside wall and the dead spot between pump inflow and outflow. Since these relatively dead spots were not large, they accumulated only bed load and not suspended load. This bed load accumulation could be observed after the tank was drained. Although large amounts of bed load were observed after the dual alkali erosion test, it is estimated that at least an order of magnitude less bed load was observed after the direct lime waste runs. Dissolution of the direct lime wastes or portions of them seems to be the only explanation of this phenomenon. This explanation seems reasonable in light of the results of the subsequent dissolution tests, discussed below.



Source: Arthur D. Little, Inc. and New England Aquarium

FIGURE B-4 OBSERVED SUSPENDED SOLIDS LOADINGS AND TOTAL WEIGHT LOSS DURING BENTHIC EROSION STUDIES



Source: Arthur D. Little, Inc. and New England Aquarium

FIGURE B-5 CALCULATED PERCENT SUSPENDED LOADS AND MEASURED TOTAL MASS LOSSES OF TEST MATERIALS

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C. DISSOLUTION OF UNTREATED FGC WASTES AND EQUILIBRIUM TOS LEVELS

1. Description of Experiments

The maximum sulfite concentration dissolved in seawater due to the presence of FGC waste can be determined by the solubility of calcium sulfite in this medium. The factors which are expected to affect this solubility are the properties of the medium, such as the concentration of various species and total ionic strengths, and temperature. Under conditions where both of these are constant, the product of the total calcium times the sulfite levels at equilibrium are expected to be fixed. Thus, with fixed temperature and medium, the variable factor governing the soluble sulfite level is the calcium concentration. Since sulfite-rich waste materials often contain other more soluble calcium salts which may dissolve and increase the concentration of calcium in water, the equilibrium sulfite concentration may depend on the nature of the waste itself. Thus an investigation of the sulfite equilibrium level should include measurements using different types of FGC waste materials.

The dissolution process may be envisioned as a competition between the tendency for solid $CaSO_3$ molecules to become calcium and sulfite ions and the reverse reaction of Ca^{++} and $SO_3^{=}$ ions to form solid $CaSO_3$. The rate of approach of the sulfite level to the equilibrium concentration is expected to be dependent on several factors. The factors which affect the rate of dissolution of the solid will include the chemical morphology of the solid, its physical state and the ambient temperature. The reverse reaction of the ions to form the solid will be governed by the effective concentrations (activity) of calcium and sulfite ions in the liquor as well as by temperature. Thus, investigation of the rate of dissolution should also include consideration of the effect of varying solid concentrations. In the experiments described below, an attempt was made to determine the influence of this variable and variations in waste type on the equilibrium sulfite level.

a. Experimental Apparatus and Procedure

The calcium and magnesium concentrations were determined by atomic absorption spectrophotometry. Synthetic seawater was prepared from a mix obtained from Aquarium Systems, Inc. These experiments were performed with samples of wastes L1, L2, DA2 and DA3, all with sulfite-rich waste materials. The chemical composition of the as-received wastes were determined and are listed in Table B-4.

These materials were prewashed three times by slurrying the waste with equal amounts of water (wt/wt) and filtering so that the experimental results would not be affected by any remaining sulfite containing scrubber liquor.

TABLE B-4

CHEMICAL COMPOSITION OF THE AS-RECEIVED WASTES

Sludge	% Solid	Ca	TOS	$SO_4^=$	Na	Mg	OH
L1 (Direct lime, centrifuge cake, flyash)	63	4.59	3.84	0.7	0.03	0.04	--
L2 (Direct lime, filter cake, clean)	52	7.22	5.76	1.37	0.03	0.07	--
DA2 (Dual alkali, no flyash)[a]	63	7.15	5.49	0.97	0.43	0.25	1.05
DA2 (Washed)	59	--	5.90	--	--	--	0.89
DA3 (Dual alkali, with flyash)	57	4.45	2.69	0.87	0.58	0.22	--

[a] These chemical analyses are from DA1 and have been assumed to be similar for DA2. Both samples are from the same batch.

Source: Arthur D. Little, Inc.

Due to the susceptibility of very dilute solutions to sulfite oxidation, a procedure for handling and analyzing these samples was developed which minimized their contact with oxygen. The apparatus used in these studies consisted of a three-necked 100 ml round bottom flask. Nitrogen was introduced to the system via one of the necks using a dispersion tube and exited through a bubbler connected to another neck. Depending on the experiment, a nitrogen flow was introduced either through or above the sample. The third neck was used for sampling. A magnetic stirrer was needed to maintain a homogeneous suspension. A typical experiment was conducted in the following manner.

A known volume of seawater was introduced into the flask and deoxygenated for 15 minutes. A sample of waste was then added. A continuous nitrogen flow was maintained during this process. The system was sealed and the nitrogen flow stopped. Samples of the slurry were withdrawn after various times using a 15-ml pipet which had been flushed with nitrogen. During the sampling process, a nitrogen flow was maintained above the slurry. A sample of the liquid phase was obtained by centrifugation of the slurry. The 15-ml sample of the slurry was added to a 15-ml centrifuge tube which was continuously purged with nitrogen. After centrifugation, a sample of the supernatant was taken and analyzed for sulfite using a modified West Gaeke procedure (ASTM D2914-70T). Details of this procedure are given below.

b. Determination of Low Concentration of Sulfite

Reagents and Solutions

Sodium tetrachloromercurate solution (0.04 M) was prepared by dissolving (10.86 g) $HgCl_2$ and (4.68 g) NaCl. Stock pararosaniline hydrochloride solution (0.2% in 1 M hydrochloric acid) was obtained from Eastman Chemicals. Phosphoric acid (3 M) was available. The pararosaniline reagent was prepared by adding 20 ml of stock solution to 25 ml of 3 M H_3PO_4 in a total volume of 250 ml.

Formaldehyde (0.2%) was prepared by diluting 5 ml of 36-38% formaldehyde to 1 liter with water.

Standard sulfite solution (0.02 M) was prepared by dissolving 1.25 g of Na_2SO_3 in 500 ml of deoxygenated water and was standardized using iodine and sodium thiosulfate solutions. Dilute standard sulfite solution (4×10^{-4} M) was prepared by diluting 2 ml of concentrated standard (0.02 M) in 100 ml of deoxygenated water. This was prepared immediately before using and maintained under a nitrogen atmosphere while taking samples.

Nitrogen, purified, was available.

Procedure

1) Pipet 20 ml of the sodium tetrachloromercurate solution into a 50-ml volumetric flask which is protected from light by an aluminum foil cover. Deoxygenate the solution by bubbling nitrogen through it for 10 minutes.

2) Pipet 2-10 ml of sample. The sulfite is now stabilized and these samples can be stored for several hours as long as they are protected from light.

3) Prepare a set of standard stabilized solutions including a blank by adding various volumes of the dilute sulfite solution. Analyze the standard and sample solutions simultaneously according to the following steps.

4) Pipet 4 ml of the formaldehyde solution to the 50-ml volumetric flask containing the sample.

5) Add 10 ml of the pararosaniline reagent and start a laboratory timer that has been set for 30 minutes.

6) Bring all of the flasks to volume with deoxygenated distilled water.

7) After 30 minutes, determine the absorbance of the samples, standards and blank at 548 nm.

8) Prepare a standard calibration curve by plotting the absorbance of the standard versus concentration of sulfite.

c. Equipment and Procedure Verification

The stability of a test solution in the apparatus and reliability of the complete analytical procedure was determined by checking the stability of a dilute standard solution of sodium sulfite which had been carried through the complete procedure. In addition, the stability of the solution in the apparatus was checked by sampling at various times. The results are given below.

Time in Apparatus (min)	$10^4 \times [SO_3^=]$ moles/l
0	1.74
30	1.75
35	1.72
60	1.68
65	1.68
240	1.57
245	1.58

These data indicate good reproducibility for duplicate samples. The dilute solution of sulfite was stable for 1 hour in the apparatus; however, 9% of the sulfite was oxidized in 4 hours. Since all of the experiments conducted in this apparatus were of a 3-hour or less duration, the maximum error associated with the magnitude of the sulfite concentration can be estimated at 9%.

2. Results and Discussion

The results obtained for the sulfite concentration and product of the $[Ca^{++}]$ and $[SO_3^{=}]$ for the various waste materials under a variety of conditions are presented in Table B-5.

The data indicate equilibrium sulfite levels of $(1.6 - 2.4) \times 10^{-3}$ moles/liter (130 - 190 ppm) under the various conditions studied. This sulfite concentration range represents about a five-fold stoichiometric excess over the concentration of oxygen in air-saturated seawater (see following section). The average "Ksp" product in the 15-21°C range is 2.8×10^{-5}. The temperature dependence of the "Ksp" cannot be assessed since all of the obtained values are within the experimental error of the measurement. The increase in the concentration of calcium due to the dissolution process was in every case larger than the amount of sulfite dissolved by at least 50%, indicating the dissolution of other calcium salts ($CaSO_4$ and/or $Ca(OH)_2$). The extent of dissolution of the other salts appears more prominent for the dual alkali samples than for those from the direct lime system.

The rates of increase of soluble sulfite and calcium levels were monitored in experiments using 0.3% slurries of DA2 and L2 wastes in deoxygenated seawater. The data are shown in Table B-6 and plotted in Figure B-6.

The results indicate that the sulfite level reached 90% of its equilibrium value after only 15 minutes for L2 and, after 40 minutes, for DA2. The dissolution of calcium salts other than $CaSO_3$ is also indicated by these experiments, again with more dissolution from DA2 than L2 waste.

An investigation of the rate of dissolution at very low slurry concentrations (<300 ppm) was conducted by observing the effect of TOS on the dissolved oxygen concentration. This was done rather than attempting to follow the increase in sulfite concentration due to the experimental difficulties which would have been encountered in the measurements. These experiments are described below.

3. Summary and Conclusions

1) The highest sulfite concentration that was achieved in simulated seawater due to the dissolution of the sulfite-rich waste material was in the range of $(1.6 - 2.4) \times 10^{-3}$ M.

2) The rate of dissolution of waste is very dependent on the slurry concentration and stirring rate. Under conditions

TABLE B-5

$CaSO_3$ SOLUBILITY IN SEAWATER[a]

Exp.	Sample[b]	% Slurry	$[SO_3^{=}]$,M	$[Ca^{++}]$ Total M	$[Ca^{++}]$ Dissolved	$[Ca^{++}]T \times [SO_3^{=}]$	T, °C
12A-1	L1	1.2	2.3×10^{-3}	1.2×10^{-2}	2.7×10^{-3}	2.7×10^{-5}	Room temp, 21°C
12A-4	DA3	1.0	1.9×10^{-3}	1.7×10^{-2}	7.6×10^{-3}	3.2×10^{-5}	Room temp, 21°C
12A-2	L2	1.0	2.3×10^{-3}	1.4×10^{-2}	4.6×10^{-3}	3.2×10^{-5}	Room temp, 21°C
15-6	L2 (210 min)	0.3	2.4×10^{-3}	1.2×10^{-2}	2.7×10^{-3}	2.9×10^{-5}	15 ± 2
17-8	L2 (96 min)	0.3	2.3×10^{-3}	1.2×10^{2}	2.7×10^{-3}	2.8×10^{-5}	16 ± 1
18-11	DA2 (180 min)	0.3	1.6×10^{-3}	1.4×10^{-2}	4.0×10^{-3}	2.2×10^{-5}	15 ± 1

[a] Manufacturer supplied analysis:

Ca	390 ppm	(0.00 moles/ℓ), ADL analysis 360 ppm
Mg	1238	(0.052)
SO_4	2518	(0.027)
HCO_3^-	142	(0.0024)
Mn	1.2	(2.2×10^{-5})
Cl	18,400	(0.518)
Na	10,220	(0.444)
EDTA, V, Co, Fe, Cu	<0.1	
pH	8.2-8.4	ADL measured 8.3
ionic strength		(0.652 moles/ℓ)

[b] All cakes were washed three times by slurrying with equal weight of water and filtering.

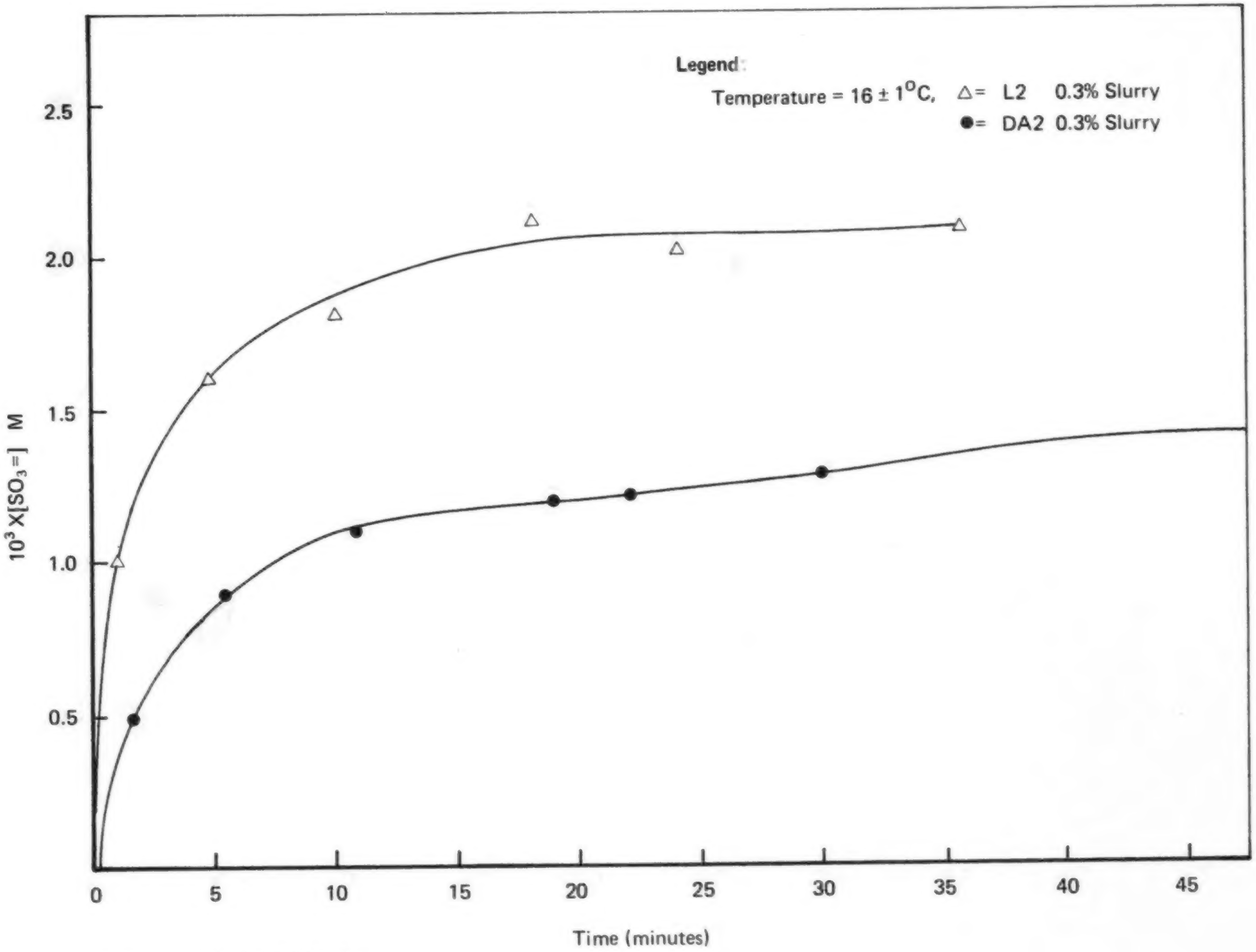
Source: Arthur D. Little, Inc.

TABLE B-6

DISSOLUTION DATA FOR SULFITE-RICH WASTES IN SEAWATER

Time (min)	$10^3 \times [SO_3^{=}]$ (moles/ℓ)	% of final value	$10^2 \times [Ca^{++}]$ (moles/ℓ)	$10^3 \times [Ca^{++}]$ INCREASE (moles/ℓ)
L2 Waste at 16°C				
0	--	--	0.9	--
1	1.0	43	1.1	2
5	1.6	70	1.3	4
10	1.8	78	1.3	4
18	2.1	91	1.2	3
24	2.0	87	1.2	3
96	2.3	100	1.2	3
D2 Waste at 16°C				
0	--	--	0.9	--
1	0.5	31	1.0	1.0
5	0.9	56	--	--
9	1.0	63	--	--
11	1.1	69	--	--
18	1.2	75	--	--
22	1.2	75	--	--
30	1.3	81	--	--
60	1.5	94	1.4	5.0
180	1.6	100	1.4	5.0

Source: Arthur D. Little, Inc.



Source: Arthur D. Little, Inc.

FIGURE B-6 DISSOLUTION RATE OF FGC WASTES IN SEAWATER of no stirring and very low slurry concentration, the rate of sulfite buildup is very low, based on the oxygen consumption.

D. EFFECT OF SULFITE-RICH WASTE ON DISSOLVED OXYGEN CONCENTRATIONS

1. Description of Experiments

The oxidation of sulfite by oxygen is known to occur according to the following stoichiometry (1):

$$2\ SO_3^{=} + O_2 \rightarrow 2\ SO_4^{=}$$

The reaction rate is very sensitive to both positive and negative catalysis, and this is a probable cause for the great difference in the experimental results of various workers. Thus, different rates have been observed depending on the source of sulfite and medium of oxidation, presumably due to the presence of trace catalysts.

Another feature which complicates the rate of dissolved oxygen (DO) consumption by sulfite due to the presence of FGC waste is the dissolution process to produce soluble sulfite. This process is affected by the several factors discussed above.

In order to estimate the effect of waste on DO concentration, it was necessary to determine the oxidation rates in the absence and presence of the dissolution process under various conditions. Factors expected to affect the dissolution and oxidation rates--such as turbulence (mixing), differences in waste materials, and differences in suspended solids levels--were considered.

In order to determine the oxidation rate in the absence of dissolution, the reaction of sodium sulfite with dissolved oxygen was studied by following the changes in concentration of both sulfite and dissolved oxygen. The effect of varying suspended solids concentration was determined by monitoring the dissolved oxygen concentration under fixed stirring conditions. The effect of turbulence was investigated by comparing data for the rate of change of DO in a stirred system to that in a simulated drop test. Finally, a comparison of behavior of the dual alkali and direct lime materials was made under similar experimental conditions.

The sulfite concentration was determined as described above for the equilibrium TOS experiments. Measurement of the dissolved oxygen concentration was made using a dissolved oxygen meter (EDC-331 dissolved oxygen analyzer, designed at Harvard University) which was standardized using air saturated seawater (7.6 ppm O_2 at 19°C) and deoxygenated seawater containing 0.1 M Na_2SO_3. The electrode was inserted into one neck of a 100-ml three-necked round bottom flask containing the test solution. The experiments were conducted by adding a known amount of waste material or solution of standard sodium sulfite to a known amount of oxygenated seawater. The system was sealed such that no gas was present above the sample and the DO concentration was monitored. The slurry samples were continually stirred at a rate which was just sufficient to keep all the particles suspended. These experiments were performed with prewashed wastes.

The effects of low suspended solids concentrations (50 - 220 ppm) on the DO concentration under conditions of very little agitation were investigated by dropping 5 g samples of waste in a 2-liter graduated cylinder containing a 40-cm column of air-saturated seawater. The seawater was agitated before the drop by pulling a metal screen through the solution. The suspended solids level produced was estimated by visual comparison with prepared standards. The DO concentration was measured 10 cm from the bottom with minimal movement of the solution. These experiments were performed with unwashed waste materials to examine the effect of remaining scrubber liquor. The dissolved oxygen electrode requires a 10-20 second response time. Thus, under conditions where the reaction time is comparable to the electrode response time, the dissolved oxygen meter readings represent only upper limits of the actual dissolved oxygen concentration.

2. Results and Discussion

The results obtained for the rate of decrease of the DO concentration due to reaction with sodium sulfite under various conditions are shown in Table B-7. The results obtained for the rate of decrease of the sulfite concentration due to reaction with dissolved O_2 at 18°C are given below:

	$\times 10^4 [SO_3^=]$ - moles/liter				
$[O_2]$, Initial	Initial	1.5 min	2.5 min	4.5 min	10 min
2.4×10^{-4} moles/l	6.1	1.8	1.7	1.7	1.6

The reaction appears to be complete within three minutes under all of the above conditions. Good agreement is observed from the results obtained using both methods of measurement. A comparison of the amounts of sulfite reacted to that of the O_2 consumed (Table B-8) also confirms the 2 to 1 stoichiometry of sulfite to O_2 in the oxidation process.

The effect of sulfite released into solution by FGC waste materials on the DO concentration was studied under various conditions. The effect of varying slurry concentrations with a fixed agitation rate was investigated for both L2 and DA3 materials. The results obtained for 75 - 2500 ppm slurries of prewashed DA2 waste containing fly ash in a continually stirred system are illustrated in Figure B-7.

The results obtained for 75 - 50,000 ppm slurries of prewashed L2 waste without fly ash under similar conditions are illustrated in Figure B-8. The dependence of the rate of oxygen consumption on the slurry concentration for the L2 waste was very similar to that of the DA 3 material under

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TABLE B-7

EFFECT OF Na_2SO_3 ON DISSOLVED OXYGEN CONCENTRATION AT 19°C

$10^4 Na_2SO_3$ Init. Conc. moles/liter	DO Electrode Reading (ppm)[a]						
	Initial	0.5 min	1.0 min	1.5 min	2.0 min	5 min	15 min
1.8	3.4	2.3	1.1	0.7	0.6	0.6	0.6
2.0	6.6	6.2	5.3	4.0	3.4	3.4	3.4
2.5	3.6	1.5	0.2	0	0	0	0
2.6	7.6	5.7	4.5	4.0	3.7	3.6	3.6
12.8	6.9	0.8	0	0	0	0	0

[a] In the case where the reaction time is comparable to the electrode response time (10-20 sec), the readings represent upper limits of the actual DO concentrations.

10 Lines to End of Typing Area

Source: Arthur D. Little, Inc.

For Page Numbering

TABLE B-8

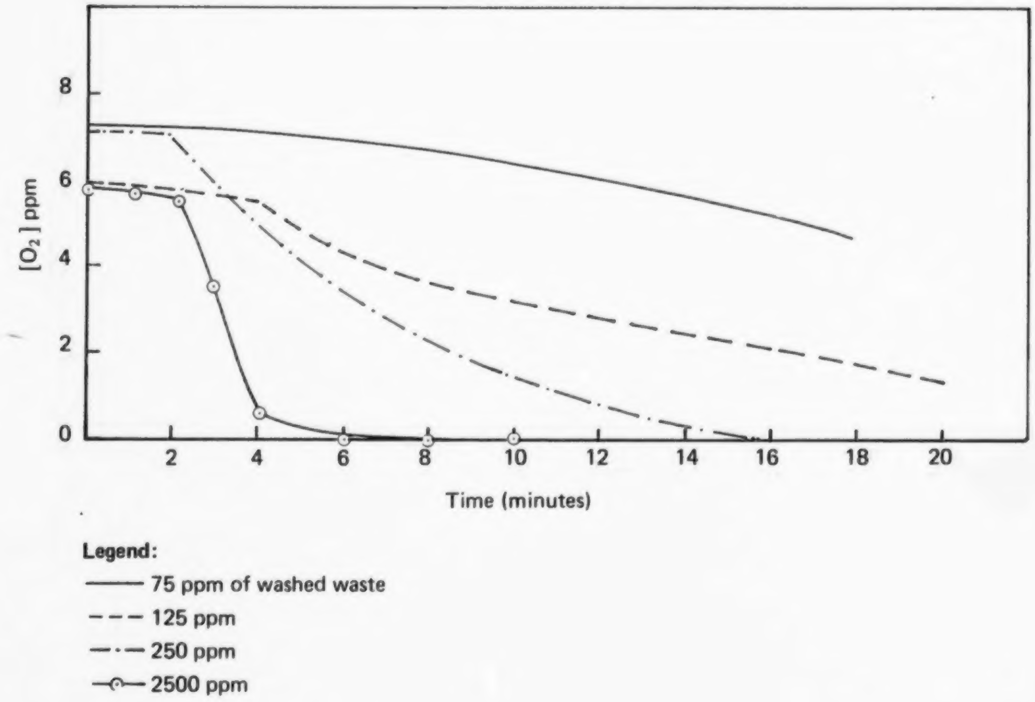
STOICHIOMETRY OF THE REACTION OF OXYGEN WITH SODIUM SULFITE

Exp.	$10^4 SO_3^=$ added	$10^4 O_2$ consumed	Stoichiometry $[SO_3] \div [O_2]$
1	1.8	0.9	2.0
2	2.0	1.0	2.0
3	2.5	1.1	2.2
4	2.6	1.2	2.1
		Average:	2.1 ± 0.1

These results are consistent with the oxidation occurring via the following stoichiometry:

$$2SO_3^= + O_2 \rightarrow 2SO_4^=$$

Source: Arthur D. Little, Inc.



Source: Arthur D. Little, Inc.

FIGURE B-7 EFFECT OF VARYING CONCENTRATIONS OF DA3 WASTE ON DISSOLVED OXYGEN CONCENTRATION AT 16°C

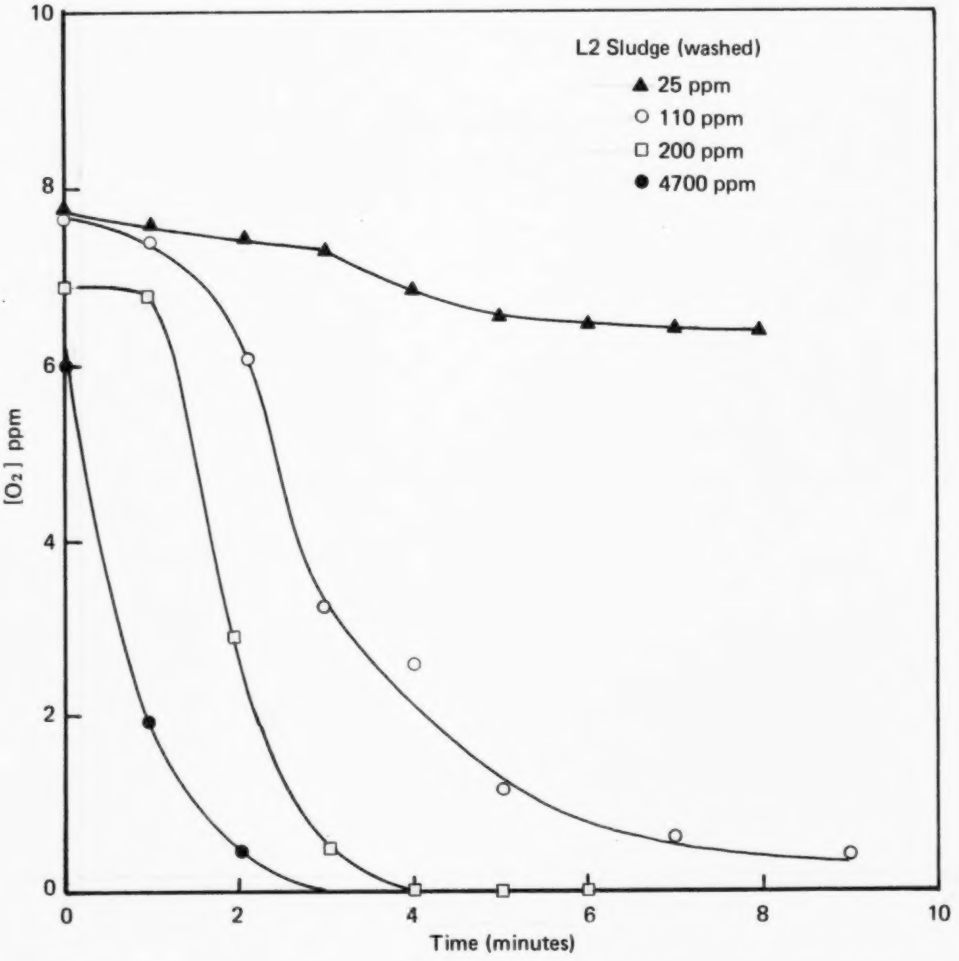


FIGURE B-8 EFFECTS OF VARYING CONCENTRATIONS OF L2 WASTE ON DISSOLVED OXYGEN CONCENTRATIONS OVER TIME

SOURCE: Arthur D. Little, Inc.

identical stirring conditions. However, the rate at a fixed slurry concentration was, in every case, about three times as fast as that observed for the DA3 waste. This difference may be due, in part, to the higher $CaSO_3$ content of the L2 material (5.7 mm/g TOS) compared to that in DA3 (2.7 mm/g TOS). The (clean) DA2 material (5.5 mm/g TOS) reacted faster than the DA3 material with fly ash, but its rate was still only about 50% of that observed for the L2. This slower reaction was also observed for the L3 direct lime material (5.89 mm/g dry TOS) obtained from a different source. This is illustrated in Figure B-9.

The rapid DO consumption observed with concentrated slurries (2500 ppm DA2 and 4700 ppm L2) are consistent with the results obtained from the dissolution data under similar conditions which indicated TOS levels exceeding the DO concentration within 1 minute for a 0.3% slurry.

The results obtained for the changes in DO concentrations for low concentrations of suspended solids in the absence of stirring (drop tests) are shown in Table B-9.

It appears that in the absence of stirring, the oxygen consumption is slower presumably because of slower dissolution. Since these measurements were made at a point in the graduated cylinder where the settling solids continued to pass, they may represent the worst "water column" situation at this experimental scale. It would also appear that if any sulfite-containing liquor was present in these solids, the amount released during the drops was not sufficient to be observed in the DO measurement.

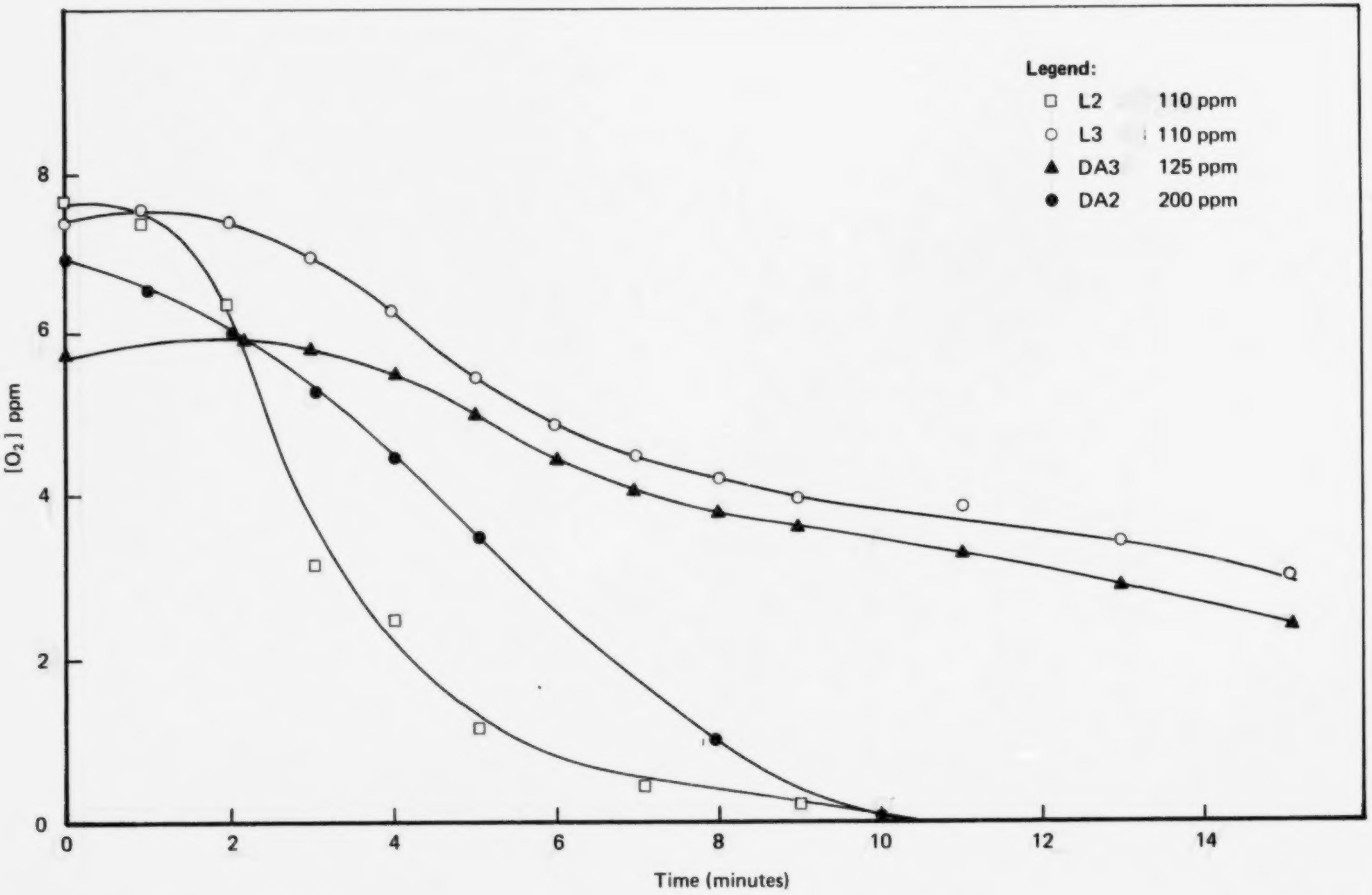
3. Summary and Conclusions

The results of these experiments may be summarized as follows:

1) The reaction of sulfite with dissolved oxygen is complete within three minutes in the sulfite concentration range $\sim 10^{-4}$ M in seawater. Thus, DO consumption is expected to be rapid as soon as the sulfite reaches that level.

2) Consumption of DO during the dumping process would be slow in the presence of waste concentrations of the same order of magnitude obtained in "drop tests" and in the absence of much agitation in the upper layers of the ocean. The extent to which such conditions could prevail at "field scale" has not been determined.

3) Due to the high waste concentrations that could occur in the areas of the ocean bottom subject to limited mixing, these areas would stand a good chance of becoming anoxic if used for conventional disposal of sulfite-rich materials.



Source: Arthur D. Little, Inc.

FIGURE B-9 COMPARISON OF DO CONSUMPTION FOR DIFFERENT FGC WASTES

TABLE B-9

DO MEASUREMENTS FOR DROP TESTS

Material	Estimated Suspended Solids Level[a]	Initial	5 min	10 min	15 min	20 min	25 min
L1 (lime, flyash)	50 ppm	7.4	7.4	7.4	--	--	--
L1 (lime, flyash)	100 ppm	7.0	6.9	6.9	--	--	--
L2 (lime, no ash)	200 ppm	7.2	7.2	7.0	6.5	6.2	6.0
DA2 (dual alkali, no ash)	150 ppm	7.5	7.5	7.3	7.0	6.5	--

[a] Based on visual comparison with prepared samples.

Source: Arthur D. Little, Inc.

APPENDIX C

DERIVATION OF A SIMPLE MATHEMATICAL MODEL FOR THE SHORT-TERM MOTION OF OCEAN DISPOSED FGC WASTES

INTRODUCTION

Outlined below is the derivation of a simple mathematical model describing the fall of ocean-disposed FGC sludge through the water column. Although many mathematical models of similar phenomena have been formulated, none has taken the approach utilized here, an approach motivated by observations of the behavior of FGC sludges during simulated disposals in the laboratory (Appendix C). The basic assumptions underlying this model are listed below:

- The entire volume of FGC sludge (typically 3000 m^3), when dropped from an open bottom barge, is assumed to break up immediately into a discrete number of sludge masses of approximately equal size.
- Each discrete sludge mass is assumed to fall through the water column as if it were unaffected by the other sludge masses around it.
- Each discrete sludge mass undergoes surface erosion as it falls.
- This eroded material is assumed to remain suspended in the water column at the depth where it is eroded and to contribute to the suspended solids level at this depth.
- The individuality of various FGC sludges is recognized in the model which requires, as an input, several proportionality constants which must be determined empirically. These constants have been determined in the laboratory for several sludges and are observed to vary from one sludge to another.
- Dissolution is ignored.

The assumptions outlined above are violated if density current effects are observed to be significant. For this reason, the model derived below is considered valid only when applied to lime sludges like the L1 and L2 wastes tested, and cannot accurately describe the behavior of all FGC wastes tested. The applicability of this model and its shortcomings are discussed further in the main text of this report.

The following derivation proceeds step by step. A listing of major symbols and their definitions follows the derivation. Major assumptions are denoted by asterisk in the left hand margin.

Velocity of a Discrete Sludge Mass as a Function of Time

The entire volume of FGC sludge, when dropped from a bottom-dump barge, is assumed to break up immediately into a discrete number of sludge masses of approximately equal size. Consider the forces on a single discrete sludge mass as it falls through the water column. Assuming quasi-steady conditions, the motion of a discrete sludge mass is governed by a force balance in which the gravitational force on the sludge mass is balanced by its buoyancy and the surface drag as it falls. The effects of buoyancy and gravity can be combined into one body force term, F_B, the submerged weight. Hence, the governing equation for this analysis is

$$F_B\ (t) = F_D\ (t) \tag{1}$$

where F_D is the magnitude of the drag force and both forces are recognized as functions of time.

The body force, F_B, can be expressed as

$$F_B\ (t) = \rho g\ (s-1)\ V\ (t) \tag{2}$$

where ρ is the density of water, g is the acceleration of gravity, s is the specific gravity of the sludge, and V is the volume of the sludge mass.

The drag force, F_D, is commonly defined as follows:

$$F_D\ (t) = 1/2\ \rho\ C_D \upsilon^2\ (t)\ A_{xs}\ (t) \tag{3}$$

where C_D is the drag coefficient, υ is the velocity of the falling sludge mass and A_{xs} is the cross sectional area of the falling sludge mass in the plane of the horizontal. In this application, it will be

* more useful to define F_D in terms of A, the total surface area of the falling sludge piece. Assuming that the sludge piece maintains the same geometry and orientation as it falls, and that C_D is constant (independent of time), we obtain

$$F_D\ (t) = \rho\ K_1 \upsilon^2\ (t)\ A\ (t) \tag{4}$$

where

$$K_1 = \frac{C_D}{2} \cdot \frac{A_{xs}(t)}{A(t)} \tag{5}$$

and K_1 is not a function of time.

Hence, substituting equations (2) and (4) into equation (1), we obtain our governing equation:

$$\upsilon(t) = \left[\frac{g(s-1)\,V(t)}{K_1\,A(t)}\right]^{1/2} \tag{6}$$

Erosion Rate of a Discrete Sludge Mass as a Function of Time

By definition, the erosion rate, E, is expressed as

$$E(t) = \frac{-d\,V(t)}{dt} \tag{7}$$

* We assume here that the erosion rate is proportional to A and to υ^2, or

$$E(t) = K_2\,A(t)\,\upsilon^2(t) = \frac{-d\,V(t)}{dt} \tag{8}$$

where K_2 has units of time/length.

Utilizing equations (6) and (8) and eliminating υ, we obtain a governing differential equation for the volume of a discrete sludge mass as a function of time:

$$\frac{K_2\,A(t)\,g\,(s-1)}{K_1\,A(t)}\quad V(t) = \frac{-d\,V(t)}{dt} \tag{9}$$

or

$$V = V_o e^{-\left[\frac{K_2\,g\,(s-1)}{K_1}\right] t} \tag{10}$$

Similarly, for the erosion rate,

$$E = K_2\,A_o\,V_o^{\,2}\;e^{-\left[\frac{K_2\,g\,(s-1)}{K_1}\right] t} = E_o e^{-\left[\frac{K_2\,g\,(s-1)}{K_1}\right] t} \tag{11}$$

In the above equation, E_o and V_o are the erosion rate and the volume, respectively, of a discrete falling sludge mass at $t={}^0$, i.e., at the surface immediately following disposal. Note that both the erosion rate and the volume decrease with time.

Erosion Rate and Velocity of a Discrete Sludge Mass as a Function of Depth

Equation (11) gives the erosion rate as a function of time. It would be more useful to have E, the erosion rate, as a function of depth. The depth of the falling sludge mass as a function of time can be obtained from equation (6) as follows:

$$\frac{dz}{dt} = \upsilon\ (t) = \left[\frac{g\ (s-1)\ V\ (t)}{K_1\ A\ (t)}\right]^{1/2} \tag{6}$$

Note that equation (6) involves the ratio of V (t) to A (t). For a sludge piece that maintains a constant geometry as it falls, it can be shown that

$$\frac{V\ (t)}{A\ (t)} = K_3\ V^{1/3}\ (t) \tag{12}$$

where K_3 is a proportionality constant, dependent on the actual geometry. Substituting equations (12) and (10) into equation (6) yields

$$\frac{dz}{dt} = \upsilon\ (t) = \left[\frac{g\ (s-1)\ K_3\ V_o^{1/3}}{K_1}\right]^{1/2} e^{-\left[\frac{K_2\ g\ (s-1)}{6K_1}\right] t} \tag{13}$$

Integrating and using the initial conditions, z = 0 at t = 0, the following equation is obtained:

$$z = \left[\frac{g\ (s-1)\ K_3\ V_o^{1/3}}{K_1}\right]^{1/2} \left[\frac{6K_1}{K_2\ g\ (s-1)}\right] \cdot \left[1 - e^{-\left[\frac{K_2\ g\ (s-1)}{6K_1}\right] t}\right] \tag{14}$$

Note that in the limit as t → ∞, z approaches a maximum value,

$$z_{max} = \frac{6}{K_2} \left[\frac{K_1\ K_3\ V_o^{1/3}}{g\ (s-1)}\right]^{1/2} \tag{15}$$

and that equation (14) can be written in terms of z_{max} as follows:

$$z = z_{max} \left[1 - e^{-\left[\frac{K_2\ g\ (s-1)}{6K_1}\right] t}\right] \tag{16}$$

Physically, equations (14) and (16) indicate that the entire discrete sludge mass erodes into the water column before falling to the depth z_{max}.

Utilizing equation (16), equation (11) can be rewritten expressing E as a function of z:

$$E\ (z) = E_o \left[1 - \frac{z}{z_{max}}\right]^6 \tag{17}$$

Similarly, equation (13) can be rewritten expressing υ as a function of z:

$$\upsilon\ (z) = \upsilon_o \left[1 - \frac{z}{z_{max}}\right] \tag{18}$$

where

$$\upsilon_o = z_{max} \left[\frac{K_2\ g\ (s-1)}{6K_1}\right] = \left[\frac{g\ (s-1)\ K_3\ V_o^{1/3}}{K_1}\right]^{1/2} \tag{19}$$

Concentration of Suspended Sludge from All Sludge Pieces as a Function of Depth

Equation (17) expresses the volumetric rate of erosion of a single discrete sludge mass as a function of depth. The total solids eroded into the water column at depth z in time Δt due to the concurrent fall of many discrete sludge pieces is thus given by the following expression:

$$E\ (z) \left[fN\ \rho_s\right] \Delta t \tag{20}$$

where f is the fraction (by weight) of the sludge that is solid material, N is the number of discrete sludge pieces, and ρ_s is the density of the sludge (including water content). The total solids eroded into the water column, as represented by expression (20) are assumed to remain in the water column as suspended solids. These solids are diluted by a mass of water, the magnitude of which is given by

$$\rho\ A_c\ \upsilon\ (z)\ \ \Delta t \tag{21}$$

where A_c, the cross sectional area of the column of water diluting the sludge, is unknown.

* In this model, it is assumed that A_c is proportional to the cross sectional area of the barge, A_B:

$$A_c = K_4\ A_B \tag{22}$$

with K_4 a dimensionless constant of proportionality.

Using expressions (20) and (21) and equation (22), it is possible to derive an expression for C (z), the average concentration of suspended sludge within a column of water of cross sectional area A_c, immediately following the passage of the falling sludge pieces (the concentration of suspended solids outside of this column is assumed to be zero):

$$C\ (z) = \frac{E\ (z)\ fN\rho_s}{\rho\ A_B\ K_4\ \upsilon\ (z)} \tag{23}$$

or, utilizing equations (11) and (18),

$$C\ (z) = C_o \left[1 - \frac{z}{z_{max}}{}^{5} \right] \tag{24}$$

where

$$C_o = \frac{E_o\ f\ Ns}{A_B\ K_4\ \upsilon_o} \tag{25}$$

Utilizing equations (11) and (12) and the relationship

$$N = \frac{V_B}{V_o}\ , \tag{26}$$

we can express C_o in terms of the basic parameters:

$$C_o = \frac{K_2\ V_B\ sf}{K_4\ A_B} \left[\frac{g\ (s-1)}{K_1\ K_3\ V_o^{\ 1/3}} \right] \tag{27}$$

Expressions for z_{90} and t_{90}

It is useful to calculate z_{90}, the depth to which 10% of the disposed sludge will descend as massive pieces and above which 90% of the disposed sludge will remain suspended in the water column. The quantity z_{90} is defined by the following integral equation:

$$\int_o^{z_{90}} C\ (z)\ dz \quad = \quad .9 \int_o^{z_{max}} C\ (z)\ dz \tag{28}$$

Substituting equation (24) into equation (28), integrating and solving for z_{90}, yields the following relationship

$$z_{90} = .32\ z_{max} \qquad (29)$$

The quantity t_{90}, the time it takes for the falling sludge masses to reach z_{90}, can be calculated by solving equation (16) for t at the point $z = z_{90}$, utilizing equation (29) as necessary. This procedure yields the result that

$$t_{90} = \frac{2.3\ K_1}{K_2\ g\ (s-1)} \qquad (30)$$

Determination of the Empirical Constants

The empirical constants for several FGC sludges were determined and are presented in Table C-1.

s and f

The specific gravity, s, was estimated based on a rough laboratory analysis. The fraction of solids, f, was also determined through laboratory analysis.

K_1

The constant, K_1, is defined in equation (5) as follows:

$$K_1 = \frac{C_D}{2} \cdot \frac{A_{xs}\ (t)}{A\ (t)} \qquad (5)$$

where C_D is the drag coefficient and A_{xs} and A are the cross sectional area and surface area, respectively, of a single discrete sludge mass. * Assuming that the sludge mass is roughly spherical in shape, equation (5) reduces to

$$K_1 \simeq .1\ C_D \qquad (31)$$

The drag coefficient C_D is both a function of the quantity

$$\frac{g\ (s-1)}{\nu^2}\ V \qquad (32)$$

where ν is the kinematic viscosity of water and a function of the shape of the sludge mass.* Assuming typical values for g, s, and ν (980 cm/sec^2, 1.2, and .015 cm^2/sec), the following values of C_D are calculated**

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*Sedimentation Engineering, ASCE Manuals and Reports on Engineering Practice No. 54, 1975, edited by Vito Vanoni, pg. 23.

**Ibid

TABLE C-1

ESTIMATED EMPIRICAL CONSTANTS FOR FGC WASTES

	s	f	K_1*	K_2(sec/cm)X10^6	K_3	K_4
Dual alkali; filter cake, no ash (DA1)	1.2	.54	.04-.07	15-30	.17	3.5
Lime, vent. filter cake, no ash (L2)	1.2	.52	.04-.07	3.6	.17	3.5
Lime, centrifuge cake, with flyash (L1)	1.2	.63	.04-.07	$<.7$	.17	3.5
Dual alkali, filter cake, no ash, rewetted (DA1)	1.2	.54	.04-.07	22	.17	3.5
Direct lime, filter cake, carbide (L3)	1.2	.50	.04-.07	7.2	.17	3.5

* Dependent on the value of V_o assumed. The range given here is for a range in V_o of 4 cc through 3000 m^3.

Note: See text for explanation

Source: Arthur D. Little, Inc., estimates

V	C_D	
	Spherical Shape	Disc Shape (disc falling parallel to the horizontal)
4 cc	.4	1.05
30 cc	.5	1.05
60 cc	.5	1.05
1 m^3	.2	1.05
3000 m^3	.2	1.05

Since the volume of a descending sludge mass decreases with time due to erosion, the drag coefficient and, hence, K_1 are also functions of time. * This dependency, however, has been ignored and K_1 is assumed to remain constant at its initial value, determined at $V = V_o$. The values of K_1 used in the calculations are listed below:

V_o	Estimated K_1
4 cc	.06
30 cc	.07
60 cc	.07
1 m^3	.04
3000 m^3	.04

K_2

The constant, K_2, is defined by equation (11) as

$$K_2 = \frac{E_o}{A_o \, \upsilon_o^2} \qquad (33)$$

K_2 was determined by analyzing the laboratory data obtained during the sludge drop experiments and by carefully observing the film records of each experiment. The procedure followed in this determination is outlined below:

- The total mass (solids plus water) eroded from each discrete sludge piece (ΔM) as it fell the 67 cm length of the water column was determined using the equation

$$\Delta M = \frac{C \; V_{tank} \; \rho}{N \; (10^6) \; f} \tag{34}$$

  where C is the estimated average concentration (in ppm by weight) of suspended sludge throughout the tank immediately following the drop, V_{tank} the volume of water in the tank, ρ the density of water, f the solids fraction of the sludge, and N the number of major discrete sludge pieces that fell to the bottom, as estimated from the films.

- The volume (V_o) and the surface area (A_o) of the typical discrete sludge mass in each experiment were estimated. The length of the water column was short enough so that these parameters did not vary significantly from the top to the bottom of the tank.

- The average fall velocity (υ_o) of each typical discrete sludge mass was calculated theoretically.

- The average volumetric erosion rate (E_o) from each typical discrete sludge mass was calculated using the following equation:

$$E_o = \frac{\Delta M \; \upsilon_o}{\rho_s \; h} \tag{35}$$

  where ρ_s is the density of the sludge (solids plus water) and h the height of the water column (67 cm).

- With all the necesssary parameters defined, K_2 was then determined using equation (33).

K_3

The parameter K_3 was defined by equation (12):

$$\frac{V\,(t)}{A\,(t)} = K_3 \; V_{(t)}^{\;1/3} \tag{12}$$

For a perfect sphere, $K_3 = .21$; for a cube, $K_3 = .17$. It was recognized that the falling sludge masses would be irregular in shape, and therefore a value of $K_3 = .17$ was chosen.

K_4

The parameter K_4 was defined by equation (22):

$$A_c = K_4 A_B \tag{22}$$

The value of K_4 was estimated at 3.5, based on observations of the sludge drop experiments.

SUMMARY

A simple mathematical model has been developed capable of predicting the following physical quantities:

- $V(z)$, $\upsilon(z)$, $z(t)$: The volume and velocity of the discrete falling sludge masses, and their depth as a function of time.
- $C(z)$: The concentration of suspended sludge material in the water column immediately following the passage of the falling sludge masses.

In addition, a number of supplementary physical quantities can be determined, including z_{max}, z_{90}, and t_{90}.

The required inputs to this model are listed below:

V_B = Volume of sludge in barge

A_B = Cross sectional area of sludge in barge

V_o = Initial volume of a single discrete sludge mass

s = Specific gravity of sludge

f = Fraction (by weight) of solids in sludge

K_1, K_2, K_3, K_4 = Empirically determined constants

Values of s, f, K_1, K_2, K_3, and K_4 have been estimated for a variety of GC sludges based on laboratory data and observations. The parameters V_B and A_B are typically 3000 m^3 and 700 m^2, respectively. The parameter V_o cannot be accurately estimated at this time. Therefore, the results presented in the main text of this report are presented for a variety of possible values of V_o.

LIST OF SYMBOLS AND DEFINITIONS

A = Total surface area of a single discrete sludge mass.

A_o = Initial total surface area of a single discrete sludge mass ($t = 0$, $z - 0$).

A_{xs} = Cross-sectional area of a single discrete sludge mass.

A_B = Cross-sectional area (parallel to the horizontal) of the sludge as contained by the barge.

A_c = Cross-sectional area of the column of water diluting the sludge.

C = Concentration of sludge.

C_o = Concentration of sludge at surface ($z = 0$).

C_D = Drag coefficient.

E = Erosion rate of a single discrete sludge mass with units of volume/time.

E_o = Initial erosion rate of a single discrete sludge mass.

F_B = Body force on a discrete sludge mass incorporating the effects of buoyancy and gravity.

F_D = Drag force on a discrete sludge mass.

f = Fraction by weight of the sludge that is solid material.

g = Acceleration of gravity.

K_1 = Empirically determined constant, dimensionless.

K_2 = Empirically determined constant, with units of time/length.

K_3 = Empirically determined constant, dimensionless.

K_4 = Empirically determined constant, dimensionless.

N = Number of discrete sludge pieces in the water column immediately following a barge drop (equals V_B/V_O).

s = Specific gravity of sludge (solids plus water).

t = Time.

LIST OF SYMBOLS AND DEFINITIONS (cont)

t_{90} = The time it takes for the falling sludge masses to reach z_{90}

V = Volume of a single discrete sludge mass

V_B = Volume of sludge contained in a barge

V_o = Initial volume of a single discrete sludge mass; occurs at $z = 0$, $t = 0$

υ = Velocity of a single discrete sludge mass

υ_o = Initial velocity of a single discrete sludge mass; occurs at $z = 0$, $t = 0$

z = Depth

z_{90} = Depth to which 10% of the disposed sludge will descend as single discrete masses and above which 90% of the disposed sludge will remain suspended in the water column

z_{max} = Maximum depth to which single discrete sludge masses fall; all sludge exists at depths less than $z = z_{max}$ as suspended solids, immediately following disposal

ν = Kinematic viscosity of water

ρ = Density of water

ρ_s = Density of sludge (solids plus water)